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Development of Risk Assessment Methodology for Municipal Sludge Landfilling

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This is one of a series of reports that present methodologies for assessing the potential risks to humans or other organisms from the disposal or reuse of municipal sludge. The sludge management practices addressed by this series include land application practices, distribution and marketing programs, landfilling, incineration and ocean disposal. In particular, these reports provide methods for evaluating potential health and environmental risks from toxic chemicals that may be present in sludge. This document addresses risks from chemicals associated with landfilling of municipal sludge. These proposed risk assessment procedures are designed as tools to assist in the development of regulations for sludge management practices. The procedures are structured to allow calculation of technical criteria for sludge disposal/reuse options based on the potential for adverse health or environmental impacts. The criteria may address management practices (such as site design or process control specifications), limits on sludge disposal rates or limits on toxic chemical concentrations in the sludge.

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DEVELOPMENT OF RISK ASSESSMENT METHODOLOGY FOR MUNICIPAL SLUDGE LANDFILLING

Environmental Criteria and Assessment Office
Office of Health and Environmental Assessment
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

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This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

PREFACE

This is one of a series of reports that present methodologies for assessing the potential risks to humans or other organisms from management practices for the disposal or reuse of municipal sewage sludge. The management practices addressed by this series include land application practices, distribution and marketing programs, landfilling, incineration and ocean disposal. In particular, these reports deal with methods for evaluating potential health and environmental risks from toxic chemicals that may be present in sludge. This document addresses risks from chemicals associated with municipal sludge landfilling.

These proposed risk assessment procedures are designed as tools to assist in the development of regulations for sludge management practices. The procedures are structured to allow calculation of technical criteria for sludge disposal/reuse options based on the potential for adverse health or environmental impacts. The criteria may address management practices (such as site design or process control specifications), limits on sludge disposal rates or limits on toxic chemical concentrations in the sludge.

The methods for criteria derivation presented in this report are intended to be used by the U.S. EPA Office of Water Regulations and Standards (OWRS) to develop technical criteria for toxic chemicals in sludge. The present document focuses primarily on methods for the development of nationally applicable criteria by OWRS.

This document was externally peer reviewed and completed in 1986. Subsequent to further review by the U.S. EPA Science Advisory Board, a revised draft incorporating review comments was produced in 1987. Various scientific and editorial changes, which clarify but do not alter the overall thrust of the document, have been made since that date.

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LIST OF ABBREVIATIONS

σz	Standard deviation of the vertical concentration distance (m)
$\gamma \ell$	Density of sludge liquid (kg/ℓ)
Δh_i	Difference in total head
Δz_i	Elevation difference between grid points
θ	Degradation rate constant (year^{-1})
θ	Effective porosity (dimensionless)
θ_e	Effective porosity
λ	Degradation/decay rate parameter (day^{-1})
λ_s	Saturated zone degradation rate constant
λ_u	Unsaturated zone degradation rate constant
υ	Average windspeed (m/sec)
ψ_e	Air entry matric potential
ψ_i	Pressure head at upper grid point
ψ_{i-1}	Pressure head at lower grid point
ψ_m	Matric potential
$\frac{\partial \psi}{\partial z}$	Hydraulic gradient in the vertical direction
$\frac{\partial H}{\partial x}$	Hydraulic gradient (dimensionless)
A	Landfill area
ADI	Acceptable daily intake (mg/kg bw/day)
AWQC	Ambient water quality criteria
b	Slope of matric potential and moisture content plot (dimensionless)
B	Bulk density of soil (g/cm^3)
B/f	Soil-to-solution ratio

LIST OF ABBREVIATIONS (cont.)

BI	Background intake of pollutant from a given exposure route (mg/day)
B_s	Bulk density saturated zone
B_u	Bulk density unsaturated zone material (kg/m^3)
bw	body weight (kg)
C	Concentration of contaminant in sludge/soil mixture (mg/kg)
C	Source concentration (mg/ℓ)
C	Solution concentration (M/L^3)
C_{dry}	Dry weight concentration of contaminant in sludge (mg/kg)
C_{ET}	Effects threshold concentration
C_l	Contaminant concentration in the liquid (mg/ℓ)
Cl_i	Concentration of i in the solution (mol/m^3)
Cl_{iET}	Limiting sludge liquid concentration
Co	Input concentration
C_s	Dry weight contaminant concentration
C_{us}	Contaminant concentration exiting the unsaturated zone (mg/ℓ)
Cv	Equilibrium vapor pressure
Cv_i	Concentration of i in air (mass/volume)
c(X)i	Atmospheric concentration (µg/m^3)
D*	Molecular diffusion coefficient of a solute in porous medium
D	Dispersion coefficient (cm^2/day)
ds	Distance to property boundary (m)
D_s	Density of sludge (kg/m^3)
D_v	Drainage volume (m^3/m^2-yr)
D_w	Density of water (kg/m^3)
EC	Environmental concentration

LIST OF ABBREVIATIONS (cont.)

Eh	Oxidation reduction potential
EP	Extraction procedure
erfc	Complementary error function
ET	Evapotranspiration losses
exp	Natural logarithm exponential
f	Soil moisture content (m^3/m^3)
f_{ave}	Average moisture content of the unsaturated zone (m^3/m^3)
f_i^*	Harmonic mean moisture content between grid points
FH	Fill height (m)
f_{oc}	Fraction of organic carbon content (of soil or sludge) (dimensionless)
f_s	Saturated soil moisture content (m^3/m^3)
H	Henry's Law Constant
H'	Modified Henry's Law Constant (dimensionless)
HHAG	Human Health Assessment Group
H_i	Henry's Law Constant for i (atm-m^3/mol)
hy	Depth to groundwater (m)
I_a	Air inhalation rate (m^3/day)
I_p	Acceptable chronic pollutant intake rate (mg/day)
I_w	Total water ingestion rate (ℓ/day)
K	Hydraulic conductivity of the medium
K_i^*	Harmonic mean hydraulic conductivity between grid points
K (ψm)	Hydraulic conductivity as a function of matric potential
Kd	Distribution coefficient (ℓ/kg)
K_{oc}	Organic carbon distribution coefficient for the contaminant (ℓ/kg)

LIST OF ABBREVIATIONS (cont.)

K_{ow}	Octanol-water partition coefficient
k_{sat}	Saturated soil hydraulic conductivity (m/yr)
L	Initial moisture content of sludge (kg/kg)
L	Soil layer
L	Mixing layer height (m)
M	Mass of contaminant
MEI	Most-exposed individual
M_L	Total leachable mass (g/m^2)
Ms	Weight of sludge solids (kg/m^2)
mv	millivolt
MW_i	Molecular weight of contaminant i
n	Total porosity of cover soil (m^3/cm^3)
N	Dry weight concentration of contaminant in sludge (mg/kg)
n_a	Air-filled porosity of cover soil (cm^3/cm^3)
n_e	Effective porosity (cm^3/cm^3)
OWRS	Office of Water Regulations and Standards
P	Total pressure in the system (atm)
P	Precipitation (m^3/m^2-yr)
PB-PK	Physiologically based pharmacokinetic
pH	Acidity
P_i	Partial pressure of i above the solution (atm)
q	Steady-state flux
Q	Allowable long-term average flux (g/m^2-sec)
Q	Source/sink strength
Q	Volume of runoff (m^3)
q_{ai}	Flux during the active uncovered period for contaminant i (g/m^2-sec)

LIST OF ABBREVIATIONS (cont.)

Qf	Volumetric flow rate (m^3/sec)
q_1^*	Human cancer potency [$(mg/kg/day)^{-1}$]
q_{pc}	Postclosure flux
q_{pi}	Emission rate through landfill cover to contaminant i (g/m^2-sec)
r'	Distance from center of source to receptor (m)
R	Recharge or infiltration rate (m^3/m^2-yr)
RAC	Reference air concentration (mg/m^3)
RCRA	Resource Conservation and Recovery Act
RE	Relative effectiveness of exposure (unitless)
RF	Retardation factor (dimensionless)
RfD	Reference dose (mg/kg/day)
RL	Risk level (unitless)
RMCL	Recommended Maximum Contaminant Level
RO	Runoff (m^3/m^2-yr)
RWC	Reference water concentration (mg/ℓ)
S	Water retention parameter (cm)
S	Storage capacity of sludge (kg/kg)
S	Solids content of the sludge (kg/kg)
SL	Site length (m)
SRR	Source-receptor ratio (sec/m)
SW	Site width (m)
$t_{1/2}$	Environmental half-life
t	Time (years)
T	Time of pulse over which all contaminant will be released (years)
T	Temperature (°C)
T-20	Temperature correction factor derived empirically

LIST OF ABBREVIATIONS (cont.)

TBI	Total background intake rate (mg/day)
TC	Travel time for a contaminant through unsaturated zone
T_c	Thickness of temporary soil cover
t_c	Thickness of cover (m)
TCLP	Toxicity characteristic leaching procedure
TCVP	Toxicity characteristic vapor procedure
t_o	Pulse duration (pulse input only) (days)
T_p	Pulse time (years)
T_T	Total travel time across all layers of unsaturated zone (years)
T_u	Steady-state travel time across an unsaturated zone soil layer (years)
TW	Travel time for water (years)
V	Interstitial pore-water velocity (cm/day)
V	Vertical term for transport (dimensionless)
$\bar{V}$	Average interstitial pore-water velocity in the x direction
V_{ave}	Average velocity across the unsaturated zone (m/year)
VOA	Volatile organic aromatics
V_{W1}	Volume of water present in the fill (m^3/m^2)
V_{W2}	Volume of water present in the fill after it drains (m^3/m^2)
V_z	Seepage velocity in the vertical direction
W_s	Water content of sludge (kg/kg)
$\bar{X}$	Leachate concentration (kg/m^3)
χ	Contaminant concentration in leachate (mg/ℓ)
X_f	Peak output concentration (at the property boundary)
X_i	Initial leachate concentration (below the landfill)
X_o	Initial concentration of X

LIST OF ABBREVIATIONS (cont.)

X_o	Length or width of source (m)
X_y	Lateral virtual distance (m)
Y_i	Mole fraction of i in the gas phase (dimensionless)
ZHE	Zero-headspace extraction

1. INTRODUCTION AND DESCRIPTION OF GENERAL METHODOLOGIC APPROACH

1.1. PURPOSE AND SCOPE

This is one of a series of reports that present methodologies for assessing the potential risks to humans or other organisms from management practices for the disposal or reuse of municipal sewage sludge. The management practices addressed by this series include land application practices, distribution and marketing programs, landfilling, incineration and ocean disposal. In particular, these reports deal with methods for evaluating potential health and environmental risks from toxic chemicals that may be present in sludge. This document addresses risks from chemicals associated with municipal sludge landfilling.

These proposed risk assessment procedures are designed as tools to assist in the development of regulations for sludge management practices. The procedures are structured to allow calculation of technical criteria for sludge disposal/reuse options based on the potential for adverse health or environmental impacts. The criteria may address management practices (such as site design or process control specifications), limits on sludge disposal rates or limits on toxic chemical concentrations in the sludge.

The methods for criteria derivation presented in this report are intended to be used by the U.S. EPA Office of Water Regulations and Standards (OWRS) to develop technical criteria for toxic chemicals in sludge. The present document focuses primarily on methods for the development of nationally applicable criteria by OWRS. It is suggested that a user-oriented manual based on these methods be developed for wider use in deriving site-specific criteria for these sludge management practices. Additional uses for the methodology may exist, such as developing guidelines for local authorities for the selection of sludge management options, but these uses are not the focus of these documents and will not be discussed.

These documents do not address health risks resulting from the presence of pathogenic organisms in sludge. The U.S. EPA will examine pathogenic risks in a separate risk assessment effort. These documents also do not address potential risks associated with the treatment, handling or storage of sludge; transportation to the point of reuse or disposal; or accidental release.

1.2. DEFINITION AND COMPONENTS OF RISK ASSESSMENT

The National Research Council (NRC, 1983) defines risk assessment as "the characterization of the potential adverse health effects of human exposures to environmental hazards." In this document, the NRC's definition is expanded to include effects of exposures of other organisms as well. By contrast, risk management is defined as "the process of evaluating alternative regulatory actions and selecting among them," through consideration of costs, available technology and other nonrisk factors.

The NRC further defines four components of risk assessment: (1) Hazard identification is defined as "the process of determining whether exposure to an agent can cause an increase in the incidence of a health condition." (2) Dose-response assessment is "the process of characterizing the relation between the dose of an agent ... and the incidence of [the] adverse health effect...." (3) Exposure assessment is "the process of measuring or estimating the intensity, frequency and duration of ... exposures to an agent currently present or of estimating hypothetical exposures that might arise...." (4) Risk characterization is "performed by combining the exposure and dose-response assessments" to estimate the likelihood of an effect (NRC, 1983). The U.S. EPA has broadened the definitions of hazard identification and dose-response assessment to include the nature and severity of the toxic effect in addition to the incidence.

Figure 1-1 shows how these components are included in the development of these risk assessment methodologies for sludge management practices. The figure further shows how each methodology may be used to develop technical criteria, and how these criteria could be used or modified by the risk manager to develop regulations and permits.

1.3. RISK ASSESSMENT IN THE METHODOLOGY DEVELOPMENT PROCESS

As illustrated in Figure 1-1, the methodology development process begins by defining the management practice. Even within a given reuse/disposal option, real-world practices are highly variable, and so a tractable definition must be given as a starting point. As a general rule, this definition should include the types of practices most frequently used. That is, the definition should not be limited to ideal engineering practice, but also need not include practices judged to be poor or substandard, unless the latter are widely used. This definition, presented in Chapter 2 of this document, helps to determine the limits of applicability of the methodology and the exposure pathways that may be of concern. However, as also shown in Figure 1-1 and as discussed in Section 1.4., this definition could be modified as the methodology is applied because the methodology itself will help to define acceptable practice.

1.3.1. Exposure Assessment.

The exposure assessment step begins with the identification of pathways of potential exposure. Exposure pathways are migration routes of chemicals from, or within, the disposal/reuse site to a target organism. For those pathways where humans are the target of concern, special consideration is given to individual attributes that influence exposure potential. Individuals will differ widely in consumption and

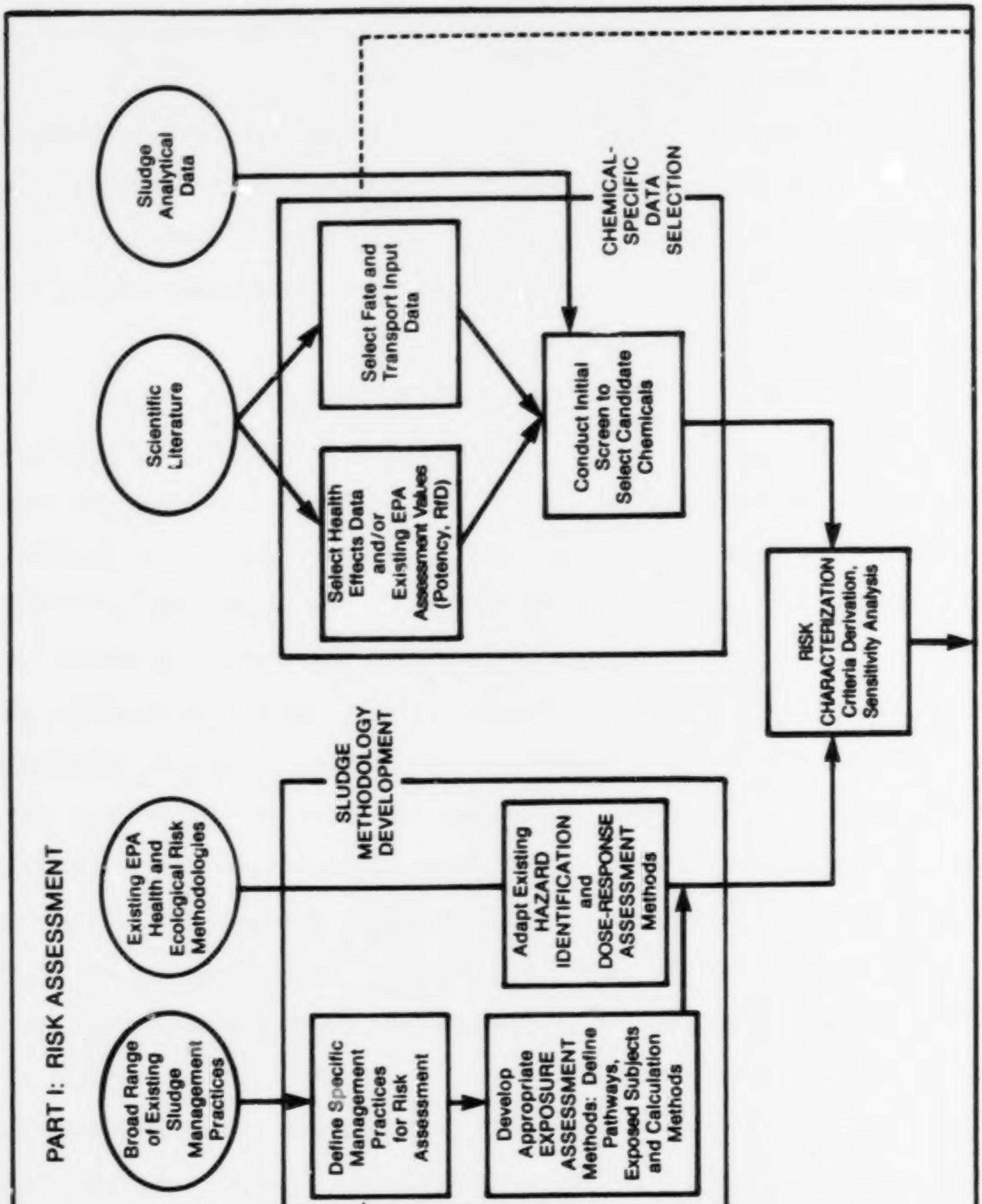
PART I: RISK ASSESSMENT
Broad Range of Existing Sludge Management Practices
Existing EPA Health and Ecological Risk Methodologies
Scientific Literature
Sludge Analytical Data
SLUDGE METHODOLOGY DEVELOPMENT
Define Specific Management Practices for Risk Assessment
Develop Appropriate EXPOSURE ASSESSMENT Methods: Define Pathways, Exposed Subjects and Calculation Methods
Adapt Existing HAZARD IDENTIFICATION and DOSE-RESPONSE ASSESSMENT Methods
Select Health Effects Data and/or Existing EPA Assessment Values (Potency, RfD)
Select Fate and Transport Input Data
CHEMICAL-SPECIFIC DATA SELECTION
Conduct Initial Screen to Select Candidate Chemicals
RISK CHARACTERIZATION Criteria Derivation, Sensitivity Analysis

FIGURE 1-1

Relationship of Risk Assessment Methodology to Other Components of Regulation Development for Sewage Sludge Reuse/Disposal Options

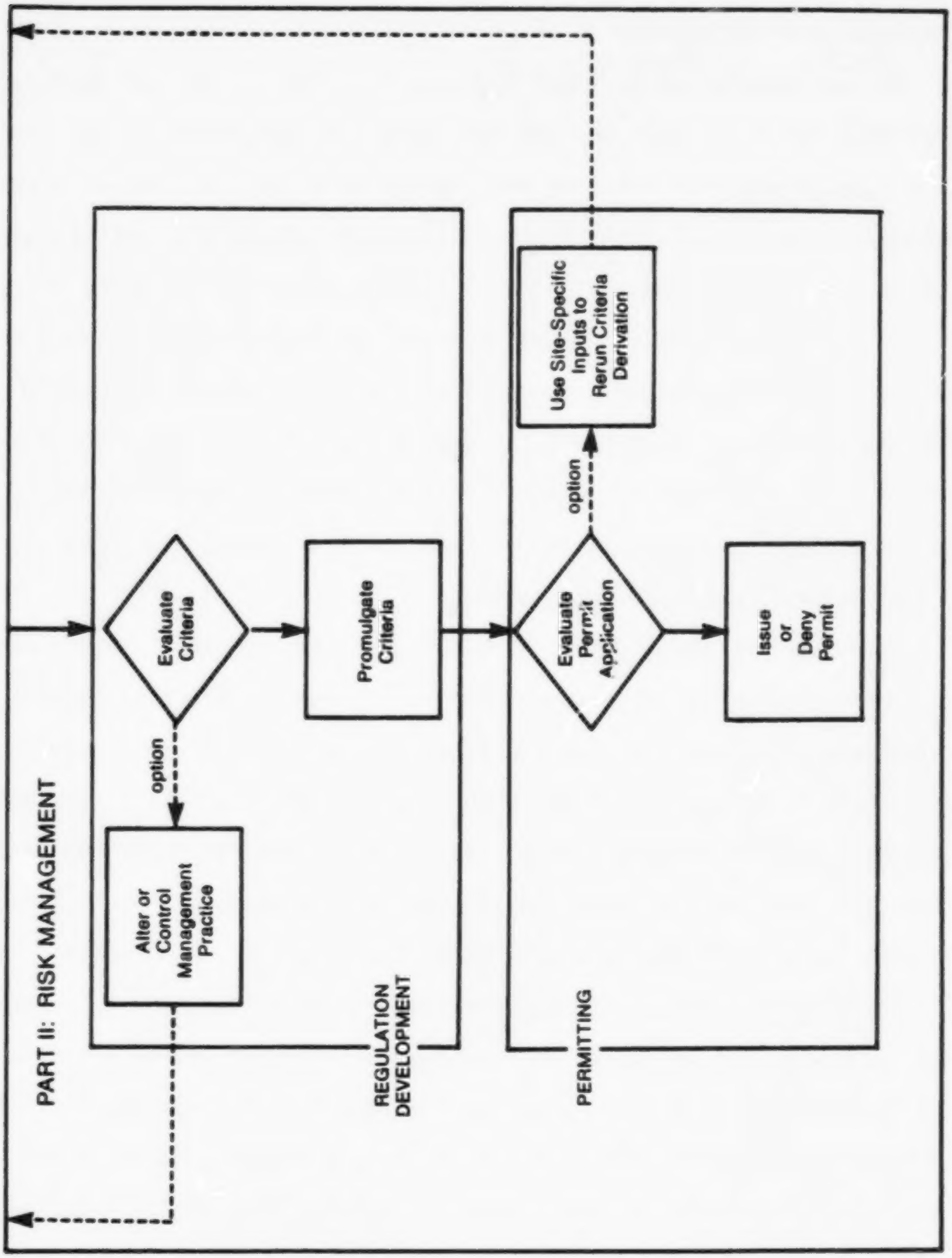
PART II: RISK MANAGEMENT
REGULATION DEVELOPMENT
Evaluate Criteria
option
Alter or Control Management Practice
Promulgate Criteria
PERMITTING
Evaluate Permit Application
option
Use Site-Specific Inputs to Rerun Criteria Derivation
Issue or Deny Permit

FIGURE 1-1 (cont.)

contact patterns relative to contaminated media, and therefore will also vary widely in their degree of exposure.

An ideal way to assess human exposure is to define the full spectrum of potential levels of exposure and the number of individuals at each level, thus quantifying the exposure distribution profile for a given exposure pathway. The methodologies described in these reports will not attempt to define exposure distributions in most cases, for the following reasons. First, it is very difficult to estimate the total distribution of exposures, because to do so requires knowledge of the distributions of each of the numerous parameters involved in the exposure calculations and also requires the modeling of actual or hypothetical population distributions and habits in the vicinity of disposal sites. Such a task exceeds the scope of the present methodology development effort.

Second, while knowledge of the total exposure distribution may be useful for certain types of decision-making, it is not necessarily required for establishing criteria to protect human health and the environment. If criteria are set so as to be reasonably protective of all individuals, including those at greatest risk, then as long as the risk assessment procedures can reasonably estimate the risk to these individuals, the quantification of lesser risks experienced by other individuals is not required.

The drawback, however, of examining only a maximal-exposure situation is that the true likelihood of such a situation occurring may be quite small. The compounding of worst-case assumptions may lead to improbable results. Therefore, the key to effective use of this methodology is a careful and systematic examination of the effects of varying each of the input parameters, using estimates of central tendency and upper-limit values in order to gain an appreciation for the variability of the result.

Therefore, exposure will be determined for a most-exposed individual, or MEI.* The definition of the MEI will vary with each human exposure pathway. Chapter 3 of this document will enumerate the exposure pathways and will define the MEI in qualitative terms; for example, for the groundwater pathway, the MEI is a person receiving all of his or her drinking water from an affected well at a landfill property boundary. The MEI will not be quantitatively defined in this chapter, but relevant information that allows the user to do so, such as available data on the ranges of drinking-water consumption rates, will be provided in later chapters. For exposure pathways concerning organisms other than humans, the term MEI is not applied, but conservative assumptions are still made regarding the degree of exposure. The remaining chapters (Chapters 4 and 5 in this document) explain the calculation methods and data requirements for conducting the risk assessments for each pathway.

1.3.2. Hazard Identification and Dose-Response Assessment. To determine the allowable exposure level for a given contaminant, the hazard identification and dose-response assessment steps must be carried out. For human health effects, these procedures already are fairly well established in the Agency, although they still require improvement and specific assessments for many chemicals remain problematic. Hazard identification in this case consists first of all in determining whether or not a chemical should be treated as a human carcinogen. Procedures for weighing evidence of carcinogenicity have been published in the U.S. EPA (1986a) and are further discussed in later sections of this document. If treated as carcinogenic, dose-response assessment would then consist of the use of Agency-accepted potency values. If none are available, cancer risk estimation procedures published by the Agency (U.S. EPA, 1986a) would be used to determine potency.

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*The definition of the MEI does not include workers exposed in the production, treatment, handling or transportation of sludge. This methodology is geared toward the protection of the general public and the environment. It is assumed that workers can be required to use special measures or equipment to minimize their exposure to sludge-borne contaminants. Agricultural workers, however, might best be considered members of the general public since the use of sludge may not be integral to their occupation.

If not carcinogenic, hazard identification and dose-response assessment normally consist of identifying the critical systemic effect, which is the adverse effect occurring at the lowest dose, and the reference dose (RfD), which is "the daily exposure ... that is likely to be without appreciable risk of deleterious effects during a lifetime" (U.S. EPA, 1988). Further description and procedures for deriving RfDs are found in U.S. EPA (1988).

For certain disposal options, effects on other organisms are of concern. In these cases, existing Agency methodologies have been used where available. For example, existing guidelines for deriving ambient water quality criteria (AWQC) (U.S. EPA, 1984d) are used to determine levels for aquatic life protection. Where effects on terrestrial species are of concern, there are no existing Agency guidelines, but suggested procedures for identifying adverse effects (hazard identification) and threshold levels (dose-response assessment) are provided.

1.3.3. **Risk Characterization.** Risk characterization consists of combining the exposure and dose-response assessment procedures to derive criteria. Risk assessments ordinarily proceed from source to receptor. That is, the source, or disposal/reuse practice, is first characterized and contaminant movement away from the source is then modeled to estimate the degree of exposure to the receptor, or MEI. Health effects for humans or other organisms are then predicted based on the estimated exposure. The calculation of criteria, however, involves a reversal of this process. That is, an allowable exposure, or an exposure that is not necessarily allowable but corresponds to a given level of risk, is defined based on health effects data, as specified above. Based on this exposure level, the transport calculations are either operated in reverse or performed iteratively to determine the corresponding source definition. In this case, the resulting source definition is a combination of management practices and sludge characteristics, which together constitute the criteria. These steps are carried out on a chemical-by-chemical basis, and criteria values are derived for each chemical assessed and each exposure pathway. An example illustrating how these calculations may be carried out is provided in this document for each pathway assessed. However, as indicated in Figure 1-1, the compilation of data on specific chemicals to be used as inputs to the methodology is a process separate from methodology development. Health effects data for individual chemicals must be collected from the scientific literature. In many cases, the U.S. EPA has already published approved values for cancer potency or RfD. Data pertinent to a chemical's fate and transport characteristics, such as solubility, partition coefficient, bioconcentration factor or environmental half-life, must also be selected from the literature. In some cases, data for particular health or fate parameters were gathered for a variety of chemicals in the process of developing the methodology. Where this was done, the information may appear as an appendix. In most cases, however, such information does not appear in the methodology documents and must be gathered as a separate effort.

Once these data have been selected, even on a preliminary basis, it may be useful to carry out a rough screening exercise, using these data plus information on occurrence in sludges, to set priorities for risk characterization. Screening could reveal that certain pollutants are unlikely to pose any risk, or that data gaps exist that preclude more detailed characterization of risk. Methods for carrying out such a screening procedure will not be discussed in this document.

Following chemical-specific data selection, risk characterization or criteria derivation may be conducted. The values derived as limits on sludge concentration or disposal rate, together with the management practice definitions, will constitute the criteria. When calculating the numerical limits, it is advisable to vary each of the input values used over its typical or plausible range to determine the sensitivity of the result to the value selected. Sensitivity analysis helps to give a more complete picture of the potential variability surrounding the result.

1.4. POTENTIAL USES OF THE METHODOLOGY IN RISK MANAGEMENT

The results of the risk characterization step can then be used as inputs for the risk management process, as shown in Part II of Figure 1-1. Although this document does not specify how risk management should be conducted, some potential further uses of the methodology in the risk management process are briefly described here. These optional steps are shown as dashed lines in Figure 1-1.

As suggested by NRC (1983), a risk manager may evalute the feasibility of a set of criteria values based on consideration of costs, available technology and other nonrisk factors. If it is felt that certain chemical concentrations specified by the calculations would be too difficult or costly to achieve, the management practice definition could be modified by imposing controls or restrictions. For example, requirement of a greater unsaturated zone thickness beneath a landfill could result in higher permissible sludge concentrations for some pollutants. The same degree of protection would still be achieved.

Following promulgation of the criteria, it may also be possible to evaluate sludge reuse or disposal practices on a site-specific basis, using locally applicable data to rerun the criteria calculations. Criteria could then be varied to reflect local conditions. Thus, the methodology can be used as a tool for the risk manager to develop and fine-tune the criteria.

1.5. LIMITATIONS OF THE METHODOLOGY

Limitations of the calculation methods for each pathway are given in the text and in tabular form in the chapters where calculation methods are presented. However, certain limitations common to all of the methods are stated here.

Municipal sludges are highly variable mixtures of residuals and by-products of the wastewater treatment process. Chemical interactions could affect the fate, transport and toxicity of individual components, and risk from the whole mixture may be greater than that of any single component. At present, these methodologies treat each chemical as though acting in isolation from all the others. It should be noted that U.S. EPA's mixture risk assessment guidelines (U.S. EPA, 1986b) caution that a great deal of dose-response information is required before a risk assessment could be quantitatively modified to account for toxic interactions. Future revisions to these documents to include consideration of interactions will most likely be limited to qualitative discussion of such interactions.

Transformation of chemicals occurring during the disposal practice, including during combustion, or following release may result in exposure to chemicals other than those originally found in the sludge. In many cases, these assessment procedures may not adequately characterize risks from these transformation products.

In addition, these methodologies compartmentalize risks according to separate exposure pathways. The use of an MEI approach, which focuses on the most highly exposed individuals for each pathway, reduces the likelihood that any single individual would receive such exposures by more than one pathway simultaneously, and therefore the addition of doses or risks across pathways is not usually recommended. However, it is possible that risk could be underestimated in a small number of instances.

Finally, the methodologies look at exposed organisms in isolation. Population-level or ecosystem-level effects that could result from a reuse or disposal practice might not be predictable by this approach.

2. DEFINITION OF DISPOSAL PRACTICES

In order to develop a risk assessment methodology for the landfilling of municipal wastewater sludges, the following general management practices are assumed.

For the present regulation, no codisposal practices will be considered. The U.S. EPA's Office of Solid Waste has initiated an effort to develop a risk assessment methodology for the codisposal of municipal sludge and municipal solid waste. While Section 405(d) of the Clean Water Act requires the U.S. EPA to regulate the disposal of sludge, including landfilling, the Resource Conservation and Recovery Act (RCRA) requires the U.S. EPA to regulate landfills, including those where nonhazardous material such as sludge is codisposed with solid refuse (U.S. EPA, 1980a). Since 95% of codisposed material is solid refuse on a weight basis, the Office of Solid Waste will be regulating codisposed sludge under Subtitle D of RCRA. Thus, this document assumes only monofills. The sludges may include digested or undigested solids from primary, secondary or tertiary treatment processes. Although undigested sludges are allowed to be landfilled, it is strongly encouraged to use digested sludges because of esthetics and potential health problems.

It is assumed that deposition occurs in a recessed trench or pit, or that the working face is surrounded by surface drainage control ditches to divert runon and capture any contained runoff. No flexible membrane liners are assumed to be installed in the landfills. Clay liners may be present. Although in some cases cover may be applied at greater intervals, cover is assumed to be applied daily and to consist of excavated soils from the trenches on site.

The addition of bulk to the sludge is not assumed. Therefore, it is assumed that sludges will contain 20-40% solids. This is necessary to support a soil cover. Since a relatively flat site could pond, and an excessively steep site could erode and create operational difficulties, sludge landfilling is usually limited to areas that have slopes >1% and <18%.

In addition to these assumed general management practices, the following practices are assumed for specific types of landfills.

In narrow trenches, sludge is assumed to be disposed in a single application with a single layer of soil applied. Excavation is accomplished by equipment based on solid ground adjacent to the trench, and the equipment does not enter the excavation. Excavated material is usually immediately applied as cover over an adjacent sludge-filled trench. Occasionally it is stockpiled alongside the trench from which it was excavated for subsequent application as cover over that trench.

Wide trenches are usually excavated by equipment operating inside the trench. Excavated material is stockpiled on solid ground adjacent to the trench from which it was excavated. Occasionally, however, it is immediately applied as cover over an adjacent sludge-filled trench. Cover thickness varies with the solids content and manner for covering. Cover is applied either by equipment based on solid, undisturbed ground adjacent to the trench or by equipment that is supported in the trench and that moves over the sludge.

Area fills have an open face on one side that may be subject to surface runoff. Drainage ditches are required in the downflow direction to contain any runoff. The water collected in the drainage ditches will either percolate into the soil or be routed to treatment. Treatment may consist of a settling pond with subsequent discharge.

When sludge is mixed with soil, it may be used as either a temporary or a final cover, or both. When mixtures are applied as final cover, the practice is most closely related to land application and should be evaluated as such. A methodology has been developed to evaluate runoff from land application of sludges.

While operating practices vary considerably, general practices can be characterized by the following:

- While 72% of the states require or can require installation of liners at landfill sites, most either do not have them or use soil-based liners with a measurable permeability.
- Cover is applied daily (often twice daily) and consists of excavated soils unless sludge/soil mixing is practiced. If the final cover uses a sludge/soil mixture, the site should be evaluated as a land application facility with respect to surface runoff.
- Deposition occurs in a recessed trench or pit, or the working face is surrounded by surface drainage control ditches to capture any contaminated runoff.
- Most sludges will contain 20-40% solids.

3. IDENTIFICATION OF KEY PATHWAYS

Based on current design and operating practice considerations, the potential routes of offsite migration can be summarized as those depicted in Figures 3-1 and 3-2:

- Vapor loss from fill material migrating from the uncovered working face and/or through the cover material and then being dispersed in the atmosphere;
- Suspension of contaminated particles from the working face with subsequent transport downwind;
- Dissolution of contaminants and/or carriage of contaminated particles in surface runoff from the working face to nearby surface waters (This pathway is not relevant to trench monofills, since the sludge is emplaced below the surface in an enclosed trench.); and
- Infiltration of water and drainage of sludge moisture transporting dissolved contaminants to the underlying aquifer.

The first two pathways threaten human health through intake of contaminated air either by onsite workers or downwind residents. The second two pathways primarily affect human health through contamination of drinking water, but may also be of concern as a result of use of contaminated water on food crops and livestock with subsequent concentration in the food chain as depicted in Figure 3-3.

3.1. GROUNDWATER INFILTRATION

Of the potential pathways, infiltration to groundwater and subsequent uptake in drinking water is considered the most significant. That determination is based both on the likelihood and the consequences of occurrence. All landfills receiving recharge will eventually allow for the generation of leachate and subsequent downward migration to groundwater. Drinking-water concentrations of pollutants established to protect human health are sufficiently low that they will be breached before water would pose a threat

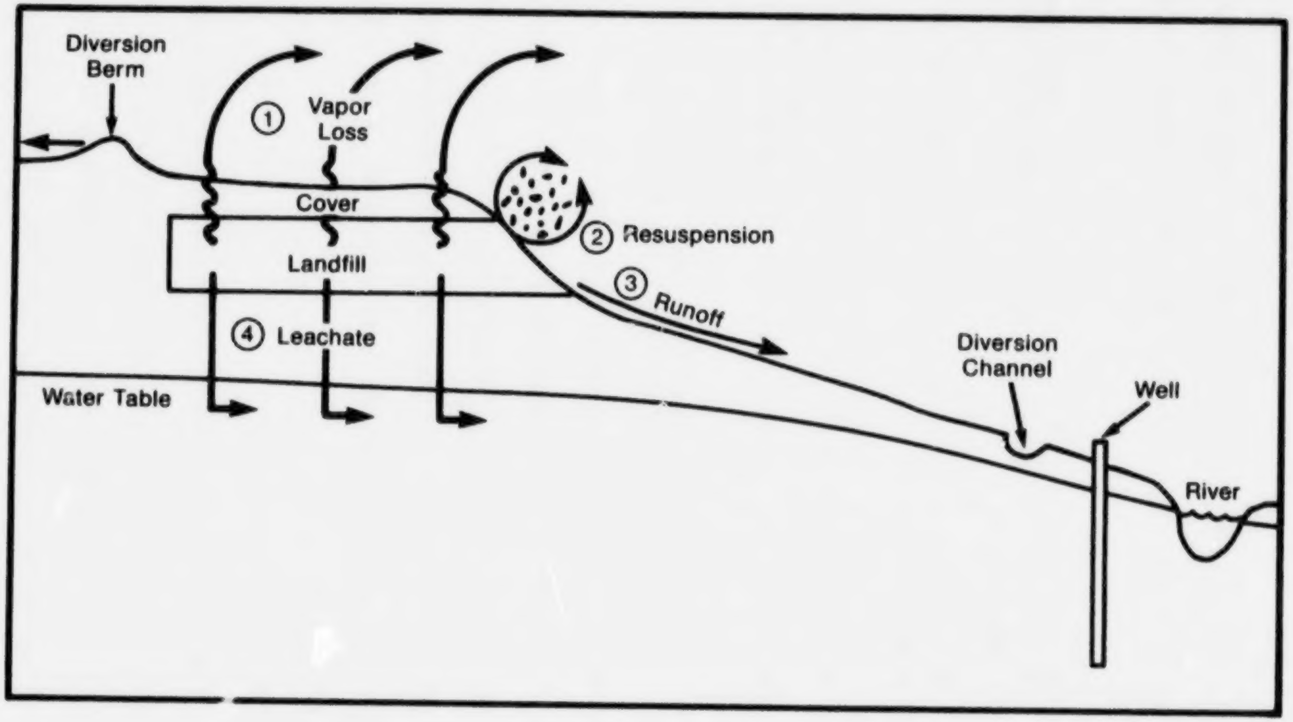
Diversion Berm
①
Vapor Loss
Cover
Landfill
② Resuspension
③ Runoff
④ Leachate
Water Table
Diversion Channel
Well
River

FIGURE 3-1

Contamination Migration Pathways for Pit or Wide Trench Landfills

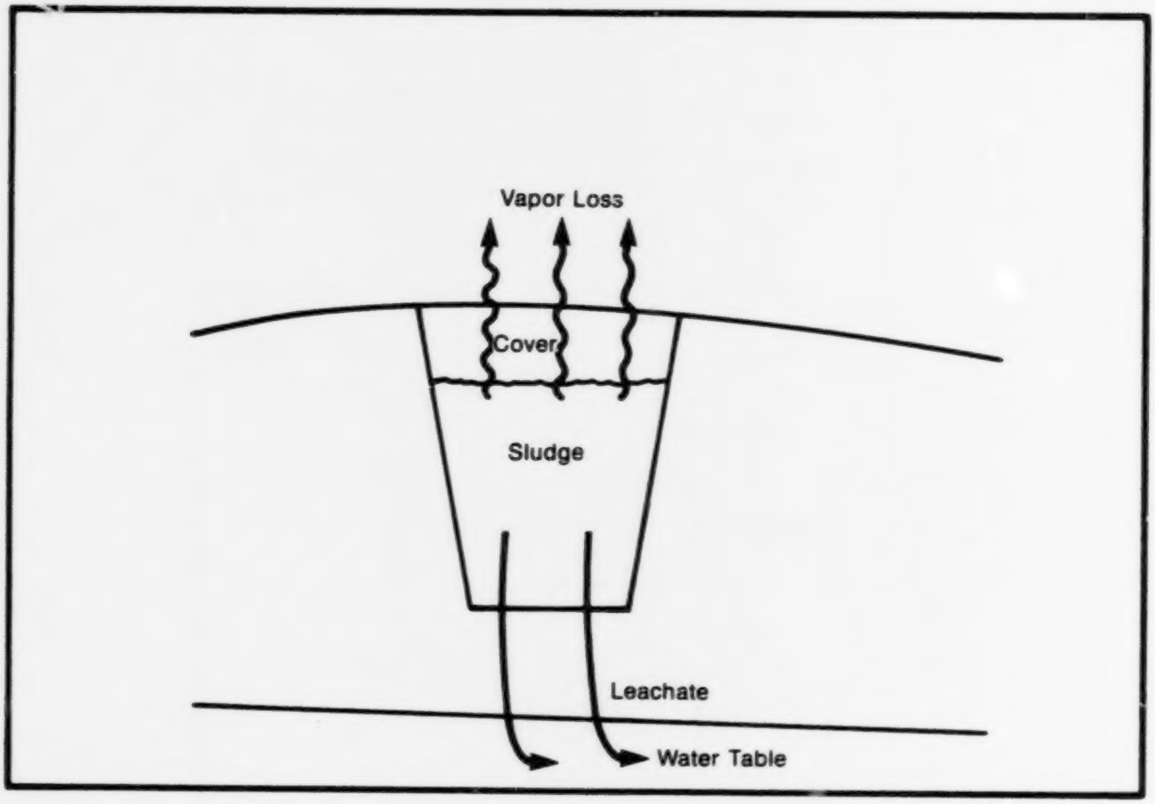
Vapor Loss
Cover
Sludge
Leachate
Water Table

FIGURE 3-2

Contamination Migration Pathways for Narrow Trench Landfills

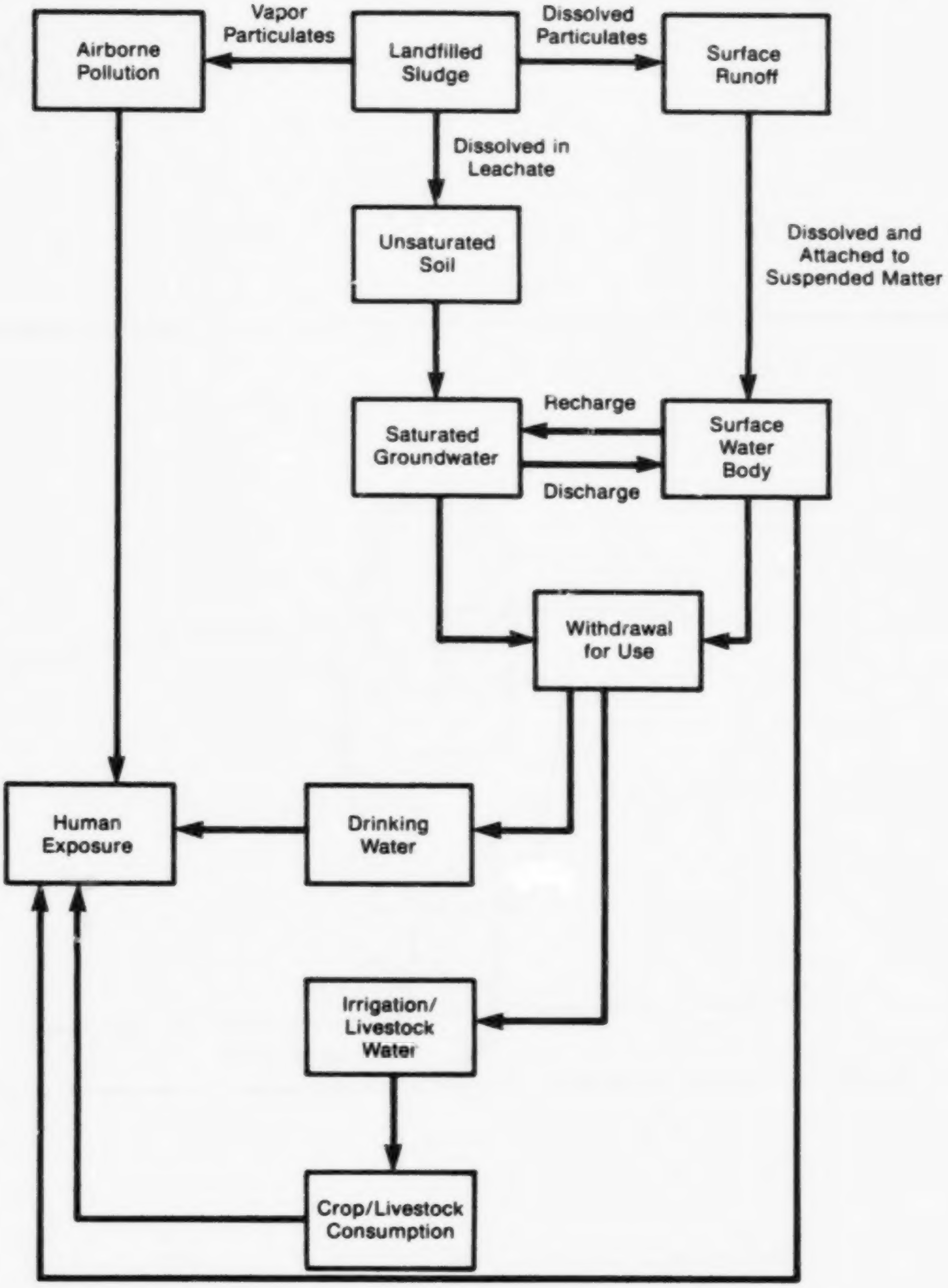
Airborne Pollution
Vapor Particulates
Landfilled Sludge
Dissolved Particulates
Surface Runoff
Dissolved in Leachate
Unsaturated Soil
Dissolved and Attached to Suspended Matter
Saturated Groundwater
Recharge
Discharge
Surface Water Body
Withdrawal for Use
Human Exposure
Drinking Water
Irrigation/ Livestock Water
Crop/Livestock Consumption

FIGURE 3-3

Possible Routes to Human Exposure from Landfilling Sludge through uptake in food-chain crops. The groundwater might be used to irrigate crops, but the sparse literature that exists on toxics uptake by plants suggests that the threat is minimal (Kowal, 1985). Therefore, risk evaluations based on drinking-water concerns will result in the most restrictive sludge concentration criteria for the groundwater pathway.

Another possible exposure route is from edible aquatic organisms living in surface water recharged by contaminated groundwater. This is considered as a supplementary groundwater pathway.

3.2. SURFACE RUNOFF

Contaminant migration in surface runoff may result from dissolution into the water or suspension of particulates to which the contaminant is attached. In either case, transport requires physical contact between the contaminant and the runoff. Therefore, contamination must be present at the soil's surface for migration to proceed by this pathway. Since clean soils are used for cover, except for the case of sludge/soil mixtures that constitute land application, the working face is the only significant source area for contaminated runoff. As noted earlier, operating procedures require control of runon and runoff from the working face with drainage ditches. In addition, since the working face is below grade for the surrounding areas, all trench or pit fills will contain runoff by design. This would not be the case for area or canyon fills, but these fills must include provisions to contain drainage in the down-gradient direction. Based on the assumption of good operating practices, runoff becomes a part of the groundwater pathway or is eliminated. The precipitation that runs off the working face will collect at the foot or in a drainage control ditch where it will either percolate into the soil, be used for dust control or be routed to treatment. In the first two cases, the runoff becomes a part of the groundwater pathway. In the third case, the pathway is terminated. Therefore, the methodology does not consider an independent surface runoff pathway.

Because good management practices will prevent the runoff pathway from being a significant route by which toxic contaminants threaten human health from sludge landfills, regulations to control this pathway are best focused on requiring those practices rather than on establishing concentration criteria. The necessary practices consist of two basic elements: (1) diversion berms and/or ditches to redirect all runon from upflow areas away from the fill area, and (2) berms and/or ditches at the foot of the fill to collect runoff from the fill area in general, and from the face in particular. These berms/ditches should be capable of containing the estimated volume of runoff from the 100-year, 24-hour design storm.

3.3. PARTICULATE SUSPENSION

The particulate suspension pathway is similar to that for surface runoff in that it requires the contaminant-bearing particulates to be at the surface where the wind and/or human activity will disturb it. The working face is the only location where this will occur to any significant extent. With daily application of cover, the face itself will not be exposed for more than 8-12 hours in any given 24-hour period. In addition, suspension will occur only when wind scour velocity exceeds a threshold value or with mechanical agitation. For soils, the scour threshold has been reported as 6-13 m/sec (Gillette, 1973). Most sludges would be expected to be on the high end of that scale or above the scale because of their moisture content and tendency to mat as they dry. Composted or dried sludges, however, may be very light and fine in texture and, therefore, easily resuspended.

While each landfill site will have its own distinct characteristic wind pattern and velocity distribution, a review of data from specific sites gives some perspective on the frequency that the threshold windspeeds will be exceeded. Table 3-1 provides data on the percent of the time that wind velocities will exceed 12 m/sec at candidate wind-generation sites. Since these sites were selected for wind-power potential, they represent the high end of the scale. In no case did 12-m/sec winds occur for >5% of the time at a 9-m height. Wind speeds diminish rapidly with proximity to the earth. Therefore, 13-m/sec speeds at a landfill working face would occur even less frequently. Thus, wind data coupled with the operating times of 50% or less without cover suggest that for windy sites, the winds will attain speeds capable of suspending sludge from the working face for brief periods of time. This will be augmented by mechanical agitation at times. In the main, particulate suspension will be episodic rather than chronic with regard to landfilled sludges.

Because particulate resuspension may occur under a limited set of conditions, it is best regulated through management practices rather than concentration criteria. In particular, resuspension shall be controlled by requiring placement of daily cover over landfilled sludges. Cover may consist of clean soils or a mixture of sludge and soil at a depth of at least 15 cm (6 in).

3.4. VOLATILIZATION

Vapor loss from sludge may result from volatilization from the uncovered working face, or release from within the fill and subsequent migration through the soil cover. The degree to which volatilization will occur depends both on the physical properties of the contaminant (e.g., vapor

TABLE 3-1

Frequency of Threshold Windspeeds for Windy Areas of the United States*

Location	Fraction of Time Wind Exceeds 12 m/sec (%)
Amarillo, TX	1.27
Block Island, RI	0.11
Boardman, OR	0.45
Boone, NC	4.98
Clayton, NM	1.73
Cold Bay, AK	4.56
Culebra, PR	1.54
Holyoke, MA	0.24
Huron, SD	0.27
Kingsley Dam, NE	0.29
Ludington, MI	1.24
Montauk Point, NY	3.51
Point Arena, CA	0.34
Russell, KS	0.84
San Goronio, CA	3.31

*Source: Adapted from Sandusky and Renne, 1981 pressure and solubility) and the nature of the sludge matrix. A strong affinity between sludge and contaminant can bind otherwise volatile contaminants and reduce losses significantly. These effects are difficult to predict a priori. Analytical methods are available to predict volatilization from soils, but they do not account for the interactions that would occur in a sludge. In general, most sludges will be subjected to thermal and mechanical action that will facilitate volatilization prior to deposition in a landfill. Subsequent release of volatile residuals, however, could occur if degradation of the sludge changed the matrix sufficiently to alter sludge contaminant interactions. The uncertainty in the rate and end products of sludge degradation in a landfill, thus, further frustrates attempts to predict vapor losses.

While placement of daily cover over sludge will reduce flux rates, preliminary calculations have revealed that vapor concentrations above reference air concentrations (see Section 5.4.3.) can be observed with sludges as a result of losses from the landfill working face prior to application of cover. Therefore, proper management through application of cover soils will not be adequate to control potential vapor problems, and concentration criteria are also required. A methodology is provided to predict vapor concentrations at the site boundary over extended periods of time in order to determine concentration criteria for volatiles.

3.5. SUMMARY

From the above considerations, it is concluded that good management practices through properly enforced regulations will control health problems stemming from contaminant transport in runoff and resuspended particulates in the atmosphere. Similar regulatory controls will not eliminate potential contaminant losses through the groundwater and vapor pathways. Therefore, contaminant concentration criteria are required to prevent infiltration and vapor losses from leading to conditions that exceed reference water and air concentrations, respectively. The following chapters describe the methodologies developed to select those criteria and quantify concentrations associated with placement of a given sludge in a designated landfill.

In all cases, use of the model and good management practices cannot guarantee that environmentally significant releases will not occur. As a consequence, a comprehensive monitoring program should be implemented with any sludge disposal alternative. In the case of landfills, this would consist of monitoring wells to detect groundwater contamination from infiltration.

4. METHODOLOGY FOR GROUNDWATER CONTAMINATION PATHWAY

4.1. OVERVIEW OF THE METHOD

As noted previously, the methodologies described herein are designed to quantify risks associated with disposal of sludges in landfills. It has been determined that the generation of leachate with subsequent migration to and contamination of groundwater is a pathway of concern. It has also been determined that the approach will be based on a risk assessment methodology that can be applied directly to input data on a given site. The merits of the proposed disposal activity will then be weighed on the basis of predicted risks to human health through drinking water. A tiered approach is offered, beginning with simple comparisons to national criteria and going to a more site-specific approach for contaminants in excess of the national criteria. The second tier allows introduction of site-specific values to reflect the conditions at the chosen site. Contaminants are considered individually in sequence. If a contaminant is not present, it is deleted and the analysis goes to the next contaminant. If a contaminant passes through below criteria, it is dropped and the next contaminant considered.

To implement such a methodology, it is necessary to simulate the movement of contaminants from the fill area through the unsaturated soil column to the aquifer and then through the saturated zone laterally out from the site. For compliance, the property boundary may be selected as the point of compliance, since drinking-water wells could be constructed from that point on and could then be affected by contamination with subsequent public health implications. In no case is the compliance point allowed to be set at a distance greater than 150 m from the landfill. Data on health effects, i.e., risk reference doses (RfDs) for noncarcinogens or potency values for carcinogens, are used to evaluate allowable levels for groundwater contamination. The premise is that a potable water supply must be maintained at healthful levels for potential future uses even if there are no current uses immediately off site.

The tiered approach begins with a comparison between measured chemical concentrations in sludge and criteria generated for a reasonable worst case landfill. Environmental setting parameters include six found to be particularly influential on water quality. The set values for five of these six parameters are as follows:

Depth to groundwater	1 m
Soil type	Sand
Recharge	0.5 m/yr
Eh - oxidation potential	+500 mv
pH - acidity	6.0

The value of the sixth parameter, partition coefficient, varies according to the chemical evaluated. The criteria are calculated using the model described herein operated to determine the sludge chemical concentration that would raise groundwater concentrations to the reference dose, but not above it.

If an operator determines that a given sludge contains chemicals exceeding the criteria used for Tier I, the operator may calculate site-specific criteria by inserting measured values for the parameters listed above and rerunning the methodology.

In either Tier I or Tier 2, the distance to the compliance point is set on the basis of the classification of the groundwater at the disposal site. If the landfill is underlain by a Class I groundwater, the compliance point is set at the point of entry, i.e., no lateral movement in the aquifer is considered. If the groundwater is Class II or III, the compliance point is set at the smaller of the two options, the fenceline or 150 m. Hence, the compliance point distance can never exceed 150 m. If the groundwater is Class III on the basis of contamination with the toxic chemical of interest, no groundwater degradation is allowed, and hence, the predicted leachate concentration must be less than or equal to the current groundwater concentration.

The tiered process is illustrated in Figure 4-1. To calculate Tier I criteria, the methodology is applied assuming a given sludge concentration. The resultant groundwater concentration is then compared with the concentration that would produce a health-based reference dose. The ratio of the two is used to recalculate until a sludge concentration is picked that will just produce the limiting groundwater concentration.

The Tier 2 process is initiated by calculating a pulse or leach time (the period of time required for all of the available contaminant to be leached from the sludge) for each contaminant. For degradable contaminants, a calculation is then made to determine how long it will take each contaminant to traverse the unsaturated zone and the amount of degradation that will take place during that time. For nondegradable contaminants, the concentration is unchanged through the unsaturated zone. For inorganic contaminants, a speciation model (MINTEQ) is used to estimate the dissolved concentration of contaminants in the saturated zone after accounting for geochemical reactions.

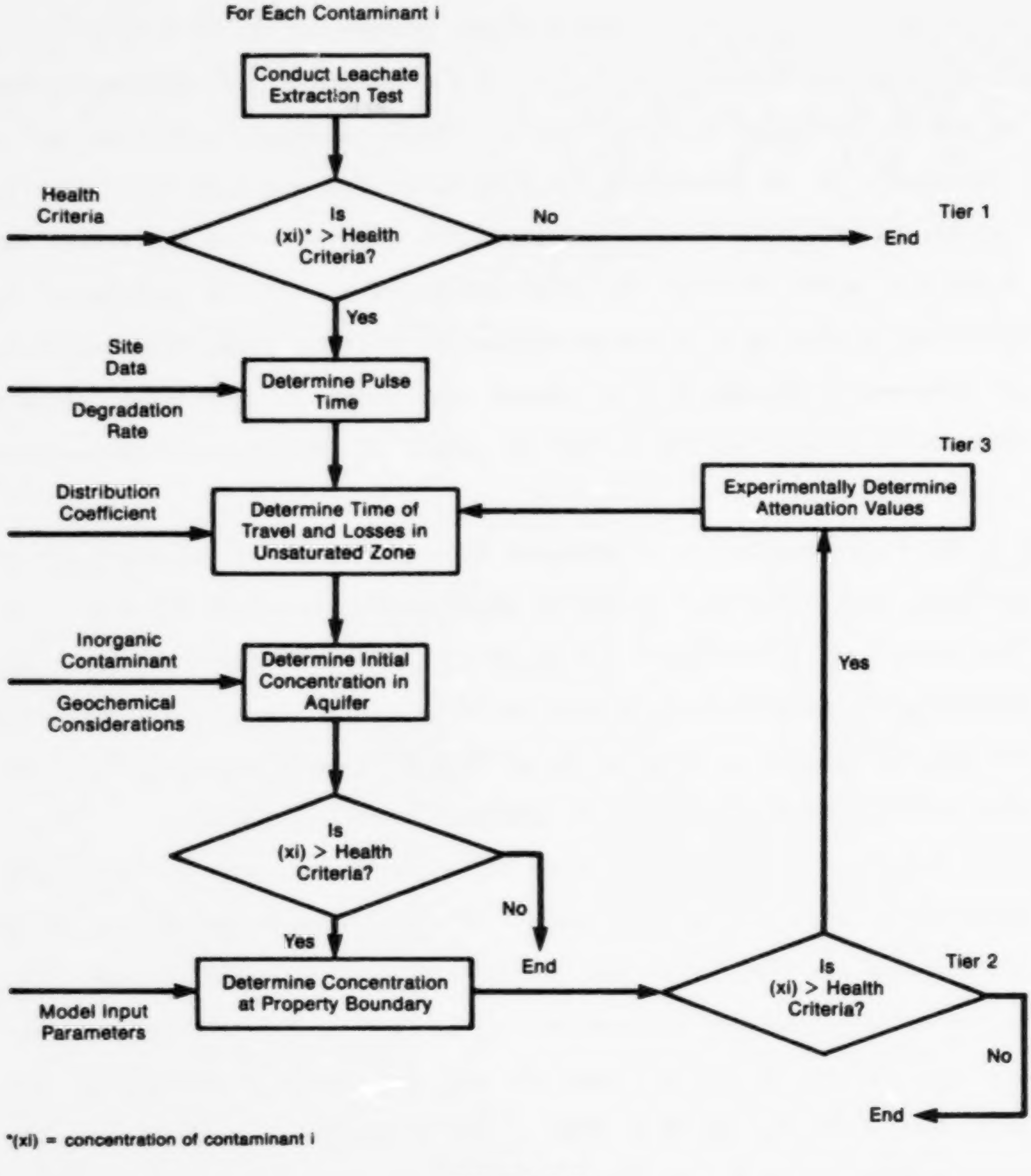
For Each Contaminant i
Conduct Leachate Extraction Test
Health Criteria
Is (xi)* > Health Criteria?
No
Tier 1
End
Yes
Site Data
Degradation Rate
Determine Pulse Time
Tier 3
Distribution Coefficient
Determine Time of Travel and Losses in Unsaturated Zone
Experimentally Determine Attenuation Values
Inorganic Contaminant
Geochemical Considerations
Determine Initial Concentration in Aquifer
Yes
Is (xi) > Health Criteria?
No
Yes
End
Model Input Parameters
Determine Concentration at Property Boundary
Is (xi) > Health Criteria?
Tier 2
No
End
*(xi) = concentration of contaminant i

FIGURE 4-1

Structure of Tiered Methodology

At this point, after accounting for degradation and geochemical reactions, a comparison is made between predicted leachate concentration entering the aquifer and the health criteria. The analysis is continued for those contaminants exceeding the health criteria.

An analytical contaminant transport model, CHAIN, is used to predict contaminant concentration at the base of the unsaturated zone. The difference between the model and the unsaturated zone calculations discussed above is that the model allows for dispersion as well as degradation. For the metals (nondegradable), the output concentrations from the model are adjusted based on geochemical reactions (MINTEQ). At this point, the model-predicted or MINTEQ-adjusted contaminant concentrations at the base of the unsaturated zone (point of entry into the aquifer) are compared to the health criteria. The analysis is continued for those that do not pass.

The final step of the analysis is to use a saturated zone transport model, AT123D, to predict contaminant concentration at the property boundary. These final contaminant concentrations at the property boundary are added to the background concentrations in the groundwater and again compared to the health criteria. If they all pass the criteria, the application would be accepted. If any one contaminant exceeds the criteria, the application would be denied. If any contaminants exceed the criteria and the analysis has been completed, then landfill disposal is not available for the sludge unless the chemical levels in the sludge are reduced. The procedures and details of each module in the methodology are described in the following sections. The methodology for calculating the contamination pathway from the groundwater to surface water to edible aquatic organisms, a supplementary pathway, is also very briefly described (Section 4.3.3.5.).

4.2. ASSUMPTIONS

In order to apply a methodology such as that presented here, it is necessary to make simplifying assumptions. The assumptions, stated or implied, required to implement the groundwater pathway analysis methodology are outlined in Table 4-1.

4.3. CALCULATIONS

4.3.1. Source Term. The sludge itself is the starting point for a contaminant's migration through the landfill and into the groundwater. Therefore, the methodology must start with the sludge. This is most simply done by assuming that the total mass of a contaminant is in dissolved form. However, such an approach is extremely conservative. Chemical-physical interactions between the organic matrix of sludge and contaminants are often quite strong and may cause immobilization of pollutants. As a consequence, not all of the contaminants in sludge are mobile. The availability of organic contaminants is often related to their concentration, so that only a fraction is mobilized at any one time. The latter is a partitioning phenomenon that controls leachate levels to a discrete ratio between concentrations in the sludge and the leachate. Current understanding of these phenomena and the effects of various constituents on them is limited, so it is not possible to accurately predict leachate levels through the use of models at this time. Inorganic contaminants may have their leachate concentrations dictated by solubility constraints.

If an applicant employs total sludge contaminant data and determines that criteria will be exceeded, an estimate of leachate quality can be derived.

TABLE 4-1

Assumptions for the Groundwater Pathway Methodology

Functional Area	Assumption	Ramifications
Source Term	Organic chemical concentrations in leachate will be determined by partitioning between organic solids in the sludge and the water as described by the K_{oc} value.	Effects would be sludge-specific. Should be very accurate when measured K_{oc} values are applied.
	Inorganic chemical concentrations in leachate will be limited to the chemical's solubility, which can be estimated from wastewater treatment plant data.	Effect is indeterminate since the presence of some chemicals will affect the ultimate solubility of the chemical of interest.
	All contaminants will ultimately be solubilized.	Overpredicts to the extent that some contaminants are irreversibly bound to solids or may react to become another chemical.
	Leachate pattern can be described as square wave.	Overpredicts duration of high concentration period, neglects presence of low concentration tail.
Unsaturated Zone Transport	One-dimensional flow in the vertical direction.	Overpredicts concentration since it ignores horizontal dispersion.
	Water flow is steady state.	Effects would be site-specific, depending on soil characteristics.
	Water table conditions at bottom of unsaturated zone.	Does not affect concentration calculations.
	Upper boundary has a constant flux.	Overpredicts concentration by accelerating timeframe over which recharge actually occurs.

TABLE 4-1 (cont.)

Functional Area	Assumption	Ramifications
Unsaturated Zone Transport (cont.)	Soil characteristics are constant with depth for any layer.	It is impossible to determine the effect of this assumption, since it will vary from site to site.
	Vertical hydraulic gradient of unity (not assumed in one of two alternative approaches).	Overpredicts concentration to the extent that gradients may be <1.0 and, therefore, time of travel is slower, allowing for more dispersion.
	Attenuation of organics is related to soil organic fraction only.	Overpredicts contaminant velocity for soils with low organic content where mineral interaction may predominate.
	All adsorption is reversible.	Overpredicts concentration arriving at aquifer.
	First-order degradation mechanism.	Underpredicts degradation where higher order rates are functional: overpredicts zero order mechanisms.
Saturated Zone Transport	Mixing depth is equivalent to the ratio of recharge to soil porosity contaminants.	Overpredicts groundwater concentration, since it does not allow for dilution of recharge into the aquifer.
	Groundwater conditions dictate geochemistry.	Effects would be site-specific depending on the quantity and quality of both the leachate and the aquifer.

TABLE 4-1 (cont.)

Functional Area	Assumption	Ramifications
Saturated Zone Transport (cont.)	The six groundwater pH-Eh couplets modeled provide an adequate set of alternatives.	Some sites could have extreme conditions beyond those modeled. If pH values are very low, the model will underpredict, and if Eh conditions are very low the model will overpredict contaminant concentrations.
	Selected organics represent leachate component.	Since the high value for organic levels in leachate was selected, the potential complexants should overpredict mobility.
	Contaminant interactions do not affect geochemistry.	Effects would be source-specific.
	Degradation is by hydrolysis only and is first order.	May overpredict concentration where chemical or biological degradation can occur.
	No organic matter resides in aquifer media and, therefore, organics are not attenuated.	Overpredicts concentration by eliminating attenuation of organics.
	No organic contaminant is present in system to start with. U.S. average prevail for inorganic contaminant background levels.	Underpredicts concentration if contaminant is present in native soils or groundwater above assumed levels.
	Input concentration is constant.	Overpredicts concentration by equaling pulse to a square wave.

For the purposes of this methodology, leachate concentrations are estimated differently for organic contaminants and inorganic contaminants. Organic concentrations in leachate are calculated using a partition coefficient, K_{oc}. The value of K_{oc} is determined as the ratio of the concentration of the chemical in the sludge to its concentration in the water associated with the sludge, i.e.:

$$K_{oc} = \frac{\text{concentration of X in sludge organic carbon (mg/kg)}}{\text{concentration of X in water (mg/}\ell\text{)}} \qquad (4\text{-}1)$$

$$= \ell/\text{kg}$$

The value for K_{oc} may be measured empirically or may be estimated from relations for solubility or octanol-water partition coefficients (Lyman et al., 1982), either of which may have been measured empirically. In any case, the relation assumes that organic contaminants will adsorb onto solid organic matter or organic coatings on solids as the primary mechanism of retention.

Inorganic concentrations in leachate are assumed to be limited by solubility constraints. In other words, it is assumed that inorganic contaminants will desorb and/or dissolve from the sludge until they reach their maximum solubility. Maximum solubility levels were estimated on the basis of the maximum effluent or leachate levels reported for U.S. wastewater treatment plants (U.S. EPA, 1985a).

In addition to determining the concentration of contaminants in leachate, source term characterization is required to estimate the time over which the contaminant will be present in the leachate, or pulse time. Sludge does not act as an infinite source of contaminants. There is a finite mass of contaminant present in the sludge that can be mobilized in leachate. For some contaminants, that mass is less than the total mass in the sludge because of irreversible adsorption or other binding mechanisms. In either event, the available mass will be released from the sludge over a discrete pulse of time. It is for that period that concerns over leachate effects on public health are real and measurable.

To calculate the pulse time, it is necessary to determine total contaminant levels in the sludge, contaminant concentrations in the leachate, sludge moisture content and recharge rate. These factors are relevant to pulse time according to:

$$Q = M \div \bar{X} \tag{4-2}$$

$$Q = RT + (L - S) \tag{4-3}$$

where:

Q = volumetric water flow of leachate for the m^2 unit area required for contaminant to be completely leached (m^3).

R = recharge or volume of infiltrate entering landfill/m^2/year (m^3/year). Can be calculated as $R = P - ET - RO$, where ET is evapotranspiration losses, RO is runoff and P is precipitation. If runoff is retained for infiltration, it should not be subtracted. RO refers only to runoff that is routed to a treatment plant or otherwise allowed to leave the site.

S = storage capacity for water in sludge defined as the "dry" water content for the sludge under normal atmospheric conditions/m^2 (m^3), i.e., the product of fill height after drainage, sludge density and moisture content divided by 1000 kg/m^3.

L = water content of sludge/m^2 at time of disposal (m^3), i.e., the product of fill height, sludge density and moisture content divided by 1000 kg/m^3.

T = time of pulse over which all contaminant will be released from the sludge (years).

M = mass of contaminant contained in a volume of sludge represented by the height of the sludge in the fill and a square meter cross section (kg), i.e., M = (height of fill x 1.0 m^3) x (density of sludge kg/m^3) x (concentration [N] of contaminant in sludge kg/kg) x (1 - moisture content).

$\bar{X}$ = average concentration of contaminant in leachate (kg/m³).

Combining Equations 4-2 and 4-3:

$$T = \frac{M - \bar{X}\,(L - S)}{\bar{X}R} \qquad (4\text{-}4)$$

For degradable contaminants, the initial mass of contaminant (M) changes with time. If a first-order decay mechanism is assumed at a degradation rate λ, Equation 4-4 becomes:

$$T = \frac{1}{\lambda}\,[\ln \frac{\bar{X}R}{\bar{X}R - \lambda M}] \qquad (4\text{-}5)$$

where:

T = pulse time (years)
λ = degradation rate constant (year⁻¹)
$\bar{X}$ = leachate concentration (kg/m³)
R = recharge or infiltration rate (m³/year)
M = mass of contaminant in sludge (kg)

Therefore, Equation 4-4 is applied for arsenic, copper, mercury, nickel, bis(2-ethylhexyl)phthalate, trichloroethylene and any other contaminant where λ = 0. For all other contaminants, Equation 4-5 is applied. In either case, the result describes the length of the pulse time (T) when leachate is adding contaminant to the unsaturated zone at the concentration calculated. Since anaerobic conditions are almost certainly likely to prevail in both the unsaturated and saturated zones beneath a landfill, anaerobic degradation rates should be used.

These formulations assume all contaminants in a sludge are ultimately mobile and that contaminant concentrations remain relatively constant in leachate until the total mass is virtually depleted. The first assumption is conservative in that it does not subtract the nonmobile fractions of contaminant. The second assumption may not be conservative in that it converts the actual contaminant concentration/time relation into a square wave (i.e., a pulse of equal height throughout its duration). Because actual leachate contaminant concentrations are likely to trail off with time, the actual pulse time will be longer, but the concentrations will be smaller. The degree of distortion arising from this assumption will depend on the nature of the actual concentration/time relation. The square wave is assumed at the landfill only. Dispersion and retardation are allowed to transform the pulse once in transit.

In summary, source term characterization consists of two steps:

1. Derive a contaminant leachate concentration by applying a partition relation for organic contaminants and a maximum solubility for inorganic contaminants.
2. Calculate a pulse time using Equation 4-4 or 4-5.

4.3.2. Unsaturated Zone Transport. As leachate is generated in the landfill, it moves vertically downward through the unsaturated zone to the uppermost aquifer. To measure the risk to water quality by contaminants in the leachate, it is necessary to determine the time of travel required to reach the aquifer and subsequent effects on contaminant concentrations. Factors affecting contaminant transport in the unsaturated zone include the physical characteristics of the soil column, infiltration or recharges and the distribution coefficient for the contaminant in that matrix.

4.3.2.1. SELECTION CRITERIA -- No one method or model for calculating time of travel in the unsaturated zone is appropriate for application to all cases. In general, two criteria are used to select a procedure for use in the sludge disposal risk methodology.

The first criterion is that the method should be generally applicable to a wide range of problems or sites. Potential sites exist across the United

States and, therefore, may be characterized by a range of values. It is impossible to select any single method that is optimal for all sites. With this in mind, methods should be selected that can be used for the wide range of values potentially encountered without requiring different approaches for each setting.

The second criterion is that the data required by the method are generally available or can be estimated, i.e., the data are typically known for most disposal sites, values can be obtained for most waste sites or accurate data for a specific site can be obtained from the literature. This criterion is important because it is not intended that expensive, specialized site studies be conducted to support an application.

4.3.2.2. GENERAL APPROACHES TO CALCULATION OF TIME OF TRAVEL -- Aside from field observations, there are two basic approaches to determining travel times in the unsaturated zone: equilibrium solutions and unsaturated flow models. Both approaches are based on the same fundamental equations, but differ in the simplifying assumptions made tc solve the equations. As a result of the simplifying assumptions, the approaches differ significantly in the time necessary to obtain a solution, in computational difficulty and in data requirements. Relative characteristics of the two approaches are summarized in Table 4-2.

Based on the above information, and given the criteria discussed for selecting methods of calculating travel time in the unsaturated zone, the use of unsaturated flow models is ruled out. Therefore, time of travel will be calculated through use of appropriate equilibrium solutions. Use of an equilibrium model necessitates assumption of steady-state as opposed to transient conditions. The effects of this requirement are minimized by the use of output to compare with chronic exposure criteria. If acute exposures

TABLE 4-2

Relative Characteristics of Equilibrium Solutions and Unsaturated Flow Modeling

Characteristic	Equilibrium Solutions	Unsaturated Flow Modeling
Computation time	Short	Medium to long
Data requirements	Low to medium	Medium to large
Complexity of solution	Simple	Complex
Time dependency	Steady state	Steady state or transient

were to be evaluated, transient analyses utilizing unsaturated flow models would be more appropriate.

Analytical solutions of travel time through the unsaturated zone are based on Darcy's equation for one-dimensional flow:

$$V_Z = K(\psi_m) \frac{\partial\psi}{\partial_Z} \qquad (4\text{-}6)$$

where:

V_Z = seepage velocity in the vertical direction

$K(\psi m)$ = hydraulic conductivity as a function of matric potential

$\frac{\partial\psi}{\partial_Z}$ = hydraulic gradient in the vertical direction

In unsaturated flow, both hydraulic conductivity and moisture content are nonlinear functions of pressure head. Hydraulic conductivity, moisture content and pressure head need not be constant throughout a soil column; however, if they are not, a direct analytical solution of Darcy's equation is not possible for unsaturated flow. In order to obtain a solution of Darcy's equation for travel time in the unsaturated zone, the following assumptions must be made:

- One-dimensional flow is in the vertical direction.
- Water flow is at steady state.
- Water-table conditions exist at the lower boundary (i.e., the water table -- the top of the saturated zone -- lies at the bottom of the unsaturated zone).
- The upper boundary has a constant flux.
- Soil characteristics (moisture content vs. matric potential and hydraulic conductivity vs. matric potential) are constant with depth.
- The hydraulic gradient is vertically down and equals unity. (Drainage is due strictly to gravity, or $\partial\psi/\partial_Z = 1$.)

The steady-state assumption and that of a constant upper boundary flux imply even infiltration over time rather than periodic storm events as is typical. While these assumptions are essential for the analytical solution, under most circumstances they overpredict velocity, thus underpredicting time of travel and time-dependent attenuation such as degradation. The water-table assumption has no effect on concentration calculations.

For nonhomogeneous soils, the constant property assumption can be approximated by dividing the soil profile into a series of homogeneous layers and performing the travel time calculation on each layer individually.

The unit gradient assumption greatly simplifies the analysis. This assumption means that the matric potential and, therefore, moisture content and hydraulic conductivity are constant with depth. Using this assumption, it is possible to directly solve for moisture content in terms of the flux through the system and saturated soil properties. Knowing the moisture content and flux, it is possible to calculate the pore-water velocity and the time of travel through the unsaturated zone. The unit gradient assumption is generally valid if gravitational forces dominate other forces (e.g., capillary forces). When invalid, this assumption overpredicts contaminant concentrations by underpredicting travel time.

If the unit gradient assumption is not made, the analytical solution to unsaturated flow becomes more complex. In this case, it is necessary to employ an iterative solution for pressure head and moisture content. This iterative solution is time consuming, but can be simplified through the use of a computer.

All analytical solutions for travel time through the unsaturated zone are one dimensional. This results in conservative estimates, since lateral dispersion would reduce the concentration of contaminant at any given point of entry. When applying these solutions to specific sites, it is important to consider the horizontal variability of soil characteristics. If soil characteristics vary spatially, the solution should be applied to the soil profile having the highest hydraulic conductivity. The solution will then yield the highest velocity and shortest travel time (e.g., worst case) for the unsaturated flow system.

In summary, analytical solutions provide a means of quickly estimating time of travel through the unsaturated zone. Several assumptions are required to perform these solutions, and no single solution is appropriate for all applications. Two analytical solutions that can be used to obtain an estimate of travel time through the unsaturated zone for many typical problems are discussed in detail in the next section.

4.3.2.3. ANALYTICAL SOLUTIONS FOR ESTIMATING TIME OF TRAVEL THROUGH THE UNSATURATED ZONE -- Two analytical solutions for calculating time of travel through the unsaturated zone are presented. The first solution assumes a unit gradient condition exists and is, therefore, the simplest. The unit gradient assumption is not made in the second solution, which allows for a variable moisture content, and, therefore, it is a little more complex. The applicability of these methods is limited owing to the simplifying assumptions used (see the previous section); however, the methods can be used in a wide range of applications to calculate estimated travel times.

The two methods provided here for estimating time of travel in the unsaturated zone are consistent with the methods recommended in the Time of Travel Manual (U.S. EPA, 1985b) developed for reviewing applications for hazardous waste landfills.

The data required by these analytical solutions for calculating travel time through the unsaturated zone are stratigraphy of the site, thickness of geologic units or soils, soil moisture characteristics for each unit or soil and steady-state flux of water/moisture in the unsaturated zone.

Stratigraphic information is necessary for determining the types of soils that are present in the unsaturated zone and for establishing the layering sequence of these soils. Stratigraphy is most often determined from logs of borings drilled at the site.

The thickness of the unsaturated zone, or layers within the unsaturated zone, establishes the distance that water/moisture must travel before it reaches the water table. This information would most likely be obtained from borings.

The soil characteristics refer to the relationship between soil moisture content (f) and matric potential (ψ_m), and the relationship between hydraulic conductivity (K) and matric potential (ψ_m). Ideally, these relationships should be measured in the laboratory using soil samples obtained from the site. If laboratory measurements are not possible, the following simple analytical relationships between pressure head and water content, and between conductivity and matric potential (Campbell, 1974), can be used:

$$\psi_m = \psi_e (f_s/f)^b \tag{4-7}$$

$$K = K_{sat}(\psi_e/\psi_m)^n \tag{4-8}$$

where:

ψ_e = air entry matric potential
f_s = saturated water content
f = field water content
K_{sat} = saturated hydraulic conductivity

b = negative one times the slope of the log-log plot of ψ_m vs. f
n = 2 + 3/b

Using these relationships, it is necessary to know only the slope of the log-log plot of ψ_m vs. f, the saturated hydraulic conductivity and the field moisture content. If experimentally derived data are not available, b can be estimated from values provided in Appendix B. The saturated hydraulic conductivity can be determined in the field or measured in the laboratory. Appendix B lists representative values of saturated hydraulic conductivity for a variety of materials.

The saturated moisture content (f_s) can also be obtained from laboratory measurements. If measurements are not possible, f_s can be estimated from the total (actual) porosity. Representative values of total porosity are given in Appendix B.

Analytical solutions of travel time assume steady-state flow of moisture through the unsaturated zone. A simple approximation of steady-state flux is to assume that it is equal to the net infiltration at the site. Net infiltration is equal to the net precipitation minus actual evapotranspiration. This information should be obtainable from weather stations or agricultural research stations.

The following solution assumes steady-state flow and a unit hydraulic gradient and employs the analytical soil moisture, pressure and conductivity relationships described earlier (Campbell, 1974). Utilizing Darcy's equation and the soil characteristic relationships described by Campbell (1974), it is possible to derive the following expression for moisture content as a function of steady-state flux (Heller et al., 1985):

$$f = \left(\frac{q}{K_{sat}}\right)^m f_s \qquad (4-9)$$

where:

q = steady-state flux

K_{sat} = saturated hydraulic conductivity

f_s = saturated moisture content

m = $1/(2b + 3)$, where b is negative 1 times the slope of the log-log plot of ψ_m vs. f, as described earlier

Using Equation 4-9, it is possible to directly calculate the steady-state moisture content of the soil. Pore-water velocity (the velocity of a water particle) is defined as:

$$V = q/f \tag{4-10}$$

Therefore, travel time for water (TW) can be calculated as the thickness of the soil layer (L) divided by the pore-water velocity:

$$TW = L/V = Lf/q \tag{4-11}$$

The above solution of travel time can be applied to single- or multiple-layered systems. For multiple layers, the above calculations are performed for each layer. The total travel time through the unsaturated zone is then equal to the sum of the travel times for each layer.

Solution of the variable moisture content case is more complex and requires division of the soil profile into a number of discrete nodes or grid points as shown in Figure 4-2. The nodes do not have to be evenly spaced, but can be variably spaced to best represent different material types (layers) if they are present. The analytical solution for this case is as follows (Jacobson et al., 1985):

$$\psi_i = \psi_{i-1} + \Delta z_i \, (q/K^* - 1) \tag{4-12}$$

where:

ψ_i = pressure head at the upper grid point

ψ_{i-1} = pressure head at the lower grid point

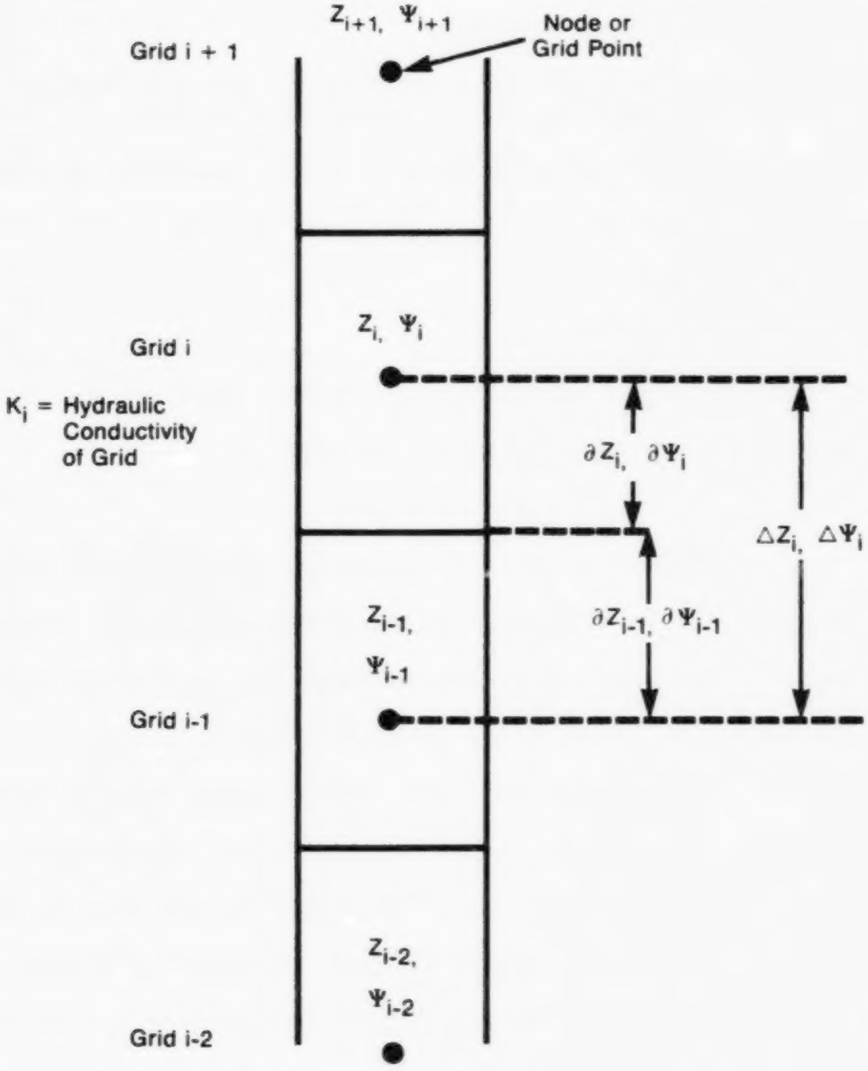
Z_{i+1}, Ψ_{i+1}
Node or Grid Point
Grid i + 1
Z_i, Ψ_i
Grid i
K_i = Hydraulic Conductivity of Grid
∂Z_i, $\partial \Psi_i$
ΔZ_i, $\Delta \Psi_i$
Z_{i-1}, Ψ_{i-1}
∂Z_{i-1}, $\partial \Psi_{i-1}$
Grid i-1
Z_{i-2}, Ψ_{i-2}
Grid i-2

FIGURE 4-2

Discretization Between Grid Points

q = flux through the soil column

Δz_i = elevation difference between grid points

K^* = harmonic mean hydraulic conductivity between grid points

$$K^* = \frac{\Delta z_i}{\delta z_i/K_i + \delta z_{i-1}/K_{i-1}} \tag{4-13}$$

K_i, K_{i-1} = hydraulic conductivity at the upper and lower grid point, respectively

The solution begins with the grid point located at the lower boundary (water table), where ψ_{i-1} is known to be zero, and K_{i-1} is known from ψ_{i-1} and the soil characteristic curve. The solution proceeds iteratively by assuming a value for ψ_i, determining K^* and then solving for ψ_i. A new value is assumed for ψ_i and the process repeated until there is convergence on a solution. The calculated value of ψ_i is then used as ψ_{i-1} for the next pair of grid points, and the process is repeated.

Once the solution has determined the pressure head at every grid point, the moisture content and hydraulic conductivity at every grid point can be obtained from soil characteristic curves. Knowing the moisture content and hydraulic conductivity at two grid points, the travel time between the grid points is given by:

$$\Delta t_i = \frac{(\Delta z_i)^2 f_i^*}{K_i^* \Delta h_i} \tag{4-14}$$

where:

f_i^* = harmonic mean moisture content between grid points

Δh_i = difference in total head

K_i^* = harmonic mean hydraulic conductivity between grid points

Δz_i = elevation difference between grid points

The above equation is used to determine the travel time between every pair of grid points. These travel time segments are then summed to obtain the total travel time through the soil column.

It is possible to perform the above solutions manually for very simple systems. However, as with all iterative solutions, the process can be very time consuming. Therefore, the use of a computer is recommended. A computer code to perform the above solutions for pressure head and travel times has been developed by Jacobson et al. (1985).

It is emphasized that soil systems are often heterogeneous. They contain a variety of materials that may create preferred routes of migration. Therefore, if field values for time of travel are available, they should be employed. Otherwise, data input to time of travel should be selected as that for the most conductive media at the site, such as the coarse sands and gravels. If the landfill includes a clay liner, the clay layer should be the upper sequence evaluated in the unsaturated zone. If a membrane liner is present, the methodology cannot be applied as described.

4.3.2.4. ESTIMATION OF CONTAMINANT TRAVEL TIME -- The analytical solutions discussed above provide an estimate of the time for leachate to travel through the unsaturated zone as a fluid. Contaminants will either travel with the leachate or at a slower velocity, depending on the degree to which they are adsorbed onto soil particles. The retardation factor is a measure of how much more slowly a contaminant moves than the bulk leachate and is a function of the contaminant/soil matrix distribution coefficient.

The retardation factor (RF) for a particular contaminant can be calculated by the formula:

$$RF = 1 + (B/f)(Kd) \qquad (4\text{-}15)$$

where:

B/f = soil-to-solution ratio (bulk density of the soil divided by its moisture content)

Kd = distribution coefficient

The Kd can be either measured in the laboratory or obtained from the literature for a wide range of soil types and contaminants. Literature values for sludge contaminants of concern are provided in Appendix B.

For organic contaminants, the Kd has been estimated using an organic carbon distribution coefficient and data on the organic carbon content of the soil. This underpredicts attenuation, since some surface adsorption also occurs on soil particles. Use of a distribution coefficient treats all adsorption as reversible. This, too, is conservative, since some sorption is irreversible and, therefore, removes contaminants permanently.

The travel time for a contaminant through the unsaturated zone (TC) can be estimated as the water travel time (TW) times the retardation factor (RF) for that particular contaminant:

$$TC = TW \times RF \qquad (4\text{-}16)$$

4.3.2.5. ESTIMATION OF CONTAMINANT CONCENTRATION -- As the leachate travels through the unsaturated zone, contaminant concentrations will be reduced through chemical and biological processes. Reductions due to precipitation of inorganic contaminants in excess of solubility limits may occur in both the unsaturated and saturated zones, but can be most easily predicted upon entry into the aquifer. As a consequence, these geochemical considerations are left to the saturated zone transport segment. Reductions due to degradation, such as hydrolysis and biochemical oxidation, will occur in the unsaturated zone. These mechanisms are characterized by a degradation rate constant (λ). This can be related to environmental half-life represented by $t_{1/2}$, the time required for the contaminant concentration to be reduced to one-half its initial value. If a first-order decay mechanism is assumed, the concentration X at any time can be defined as:

$$X = X_o e^{-\lambda t} \tag{4-17}$$

where X_o is the initial concentration of X and t is the time. Therefore, the half-life, $t_{1/2}$, can be derived as:

$$\ln \frac{X_o}{\left(\frac{X_o}{2}\right)} = \lambda t_{1/2} \tag{4-18a}$$

or

$$t\,1/2 = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda} \tag{4-18b}$$

The methodology assumes all degradation by-products are less toxic than their parent compound. This assumption will not be true for all contaminants, but it is difficult to eliminate because degradation products from a complex sludge environment have not been well characterized.

Equation 4-17 can also be employed to determine the degree of concentration reduction (degradation) that will occur as the leachate moves through the unsaturated zone. In this way, the average leachate concentration from the source ($X - X_o$) can be converted to the predicted value upon entry into the aquifer. This is done by inserting the contaminant travel time in the unsaturated zone, which is TC. From Equations 4-16 and 4-17:

$$X = X_o e^{-\lambda TC} \tag{4-19a}$$

or

$$X = X_o e^{-\left(\frac{\ln 2\ TC}{t_{1/2}}\right)} \tag{4-19b}$$

The resultant X is the contaminant concentration that should be applied to all subsequent saturated zone transport calculations. Values for the rate constant λ should be obtained from the scientific literature. If more than one degradation mechanism is applicable, a composite value, λ_t, should be derived. When all mechanisms are of the same order, the composite value is derived as the sum of the individual rate constants. The calculated values for concentration are compared to health criteria or effects thresholds. If they do not exceed the thresholds, the contaminant is dropped from further evaluation.

It is assumed that nitrogen leaches from the landfill mainly as the ammonium ion, and that negligible amounts of nitrate will be found because of the anaerobic conditions prevailing in the unsaturated and saturated zones beneath the landfill.

Use of the time of travel approach gives the reduction in contaminant concentration in the unsaturated zone due only to degradation. That is, it is conservatively assumed that the contaminant plume moves as a pulse through the unsaturated zone with no dispersion. In actuality, dispersion will cause the contaminant pulse to elongate as it moves through the unsaturated zone, with a resultant decrease in concentration. If dispersion in the unsaturated zone is expected to be significant, the applicant may wish to apply an analytical transport model to predict the concentration reduction due to dispersion.

The one-dimensional CHAIN code can be used (Van Genuchten, 1985) to estimate the effects of dispersion of contaminants in the unsaturated zone.* This code solves the convective-dispersive transport equation for a zone-dimensional case and accounts for retardation and degradation. For input data, the model requires the average pore-water velocity, the dispersion coefficient, the water content, the pulse time, the retardation factor, the decay rate and several coefficients describing the source term.

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*A more data-intensive alternative to CHAIN is the PRZM model (Carsel et al., 1984), which can produce more detailed short-term predictions; these would normally be unnecessary in the present context of chronic exposure.

The pore-water velocity can be obtained from Equation 4-10. The dispersion coefficient may be highly site specific. Where the coefficient is not known, Donigian et al. (1983) recommend a 2-fold approach for modeling dispersion in the unsaturated zone. The dispersion coefficient is at first set close to zero (0.01 cm^2/day = $3.65x10^{-4}$ m^2/year) to represent the situation where pollutant transport is convection dominated and dispersion is relatively unimportant. Next, a reasonable value is used, such as by setting the dispersion coefficient equal to one-tenth the depth to groundwater (hy) times the pore-water velocity (V). Results from these procedures are then compared to determine the potential influence of unsaturated zone dispersion. Where the latter is important, site-specific estimates may be advisable. The water content can be obtained using Equation 4-9, the pulse time from Equation 4-4 or 4-5, and the retardation factor from Equation 4-15. The source term is specified as a pulse of constant concentration as calculated by partitioning (organic contaminants) and solubility (inorganic contaminants), for a duration equal to the pulse time. Degradation rates for chemicals to be analyzed should be taken from the available literature. Care must be taken to ensure that values used are appropriate to the subsoil environment. In particular, since anaerobic conditions will prevail in the leachate-influenced unsaturated zone (as well as in the saturated zone), rates should be representative of anaerobic, rather than aerobic, systems.

The CHAIN code can be run to determine the unsaturated contaminant concentration at a depth equal to the depth to groundwater for a period equal to several contaminant travel times. The maximum resulting concentrations are compared to the effects threshold. If the maximum concentration is below the effects threshold, the analysis can be concluded without analysis of the saturated zone transport.

4.3.3. Saturated Zone Transport.

4.3.3.1. INITIAL CONCENTRATION SELECTION -- For inorganic contaminants, attenuation in soils may result from solution chemistry effects, as well as interactions with the soil matrix. In the former case, the presence of other chemical species in solution leads to the formation of insoluble salts that precipitate out as solids. At this point in the analysis, geochemistry has been accounted for only to the extent that it affects the composition of the leachate as simulated in the extraction test. While further geochemical reactions may occur as the leachate travels through the unsaturated zone, they are difficult to predict and often overshadowed by adsorption and/or exchange on particle surfaces. Therefore, they are not considered in this analysis until the leachate enters the saturated zone. The adsorption and exchange phenomena have been accounted for in selection of the unsaturated zone distribution coefficient.

It is assumed that when the leachate enters the saturated zone, it has little or no effect on the hydrology of the aquifer, i.e., leachate production is small compared to the volumetric flow of the aquifer. This will be true whenever the area of the disposal facility comprises a small fraction of the total recharge zone (a common reality). Under these circumstances, it is possible to predict solution reactions in the groundwater and subsequent solution levels for contaminants of interest. These predictions are made through the application of a geochemical model that utilizes thermodynamic data to predict equilibrium of total dissolved-phase (mobile) metal concentrations. By applying the model at this point in the analysis, it is possible to account for dissolution of salts and reduce the inventory of contaminant in leachate to those levels likely to be encountered in the aquifer. Since the final solution concentration is dictated by the solubility of product salts, considering the geochemistry in the saturated zone only and not throughout the system is not likely to have a significant impact on the results.

Geochemical models involve complex codes and massive amounts of data. The analyst must interact with the program during the analysis and, therefore, must be trained in the application of the code utilized. As a consequence, it is not the intent of this methodology to require each applicant to apply a geochemical model to site-specific conditions. Rather, a series of model runs have been made across a spectrum of conditions. Output of these runs is provided here for the applicant to utilize in selecting contaminant concentrations based on matching groundwater conditions of a given run to those of the site of interest.

The MINTEQ geochemical code was applied to generate predicted contaminant concentrations under selected groundwater conditions. MINTEQ is one of the more advanced computer codes that the U.S. EPA employs to characterize the chemical processes that may control the concentrations of constituents dissolved in leachate and natural waters. MINTEQ is a hybrid code that combines an efficient mathematical structure with a large, well-documented thermodynamic data base. Functionally, the code models the mass distribution of a dissolved element between various uncomplex and complex aqueous species; it also calculates the degree to which the water is saturated with respect to the solids in the thermodynamic data base. Adsorption, precipitation and dissolution reactions can be included in calculations. Only the latter two were applied here, since a Kd is used in the unsaturated model to address adsorption. Detailed documentation of the MINTEQ code and data can be found in Felmy et al. (1983, 1984) Morrey (1985) and Deutsch and Krupka (1985).

Each element will exist in the subsurface environment as a relatively complex distribution of different species, each having a specific set of properties. Relative concentrations of individual species within the distribution are controlled by equilibrium constants governing the individual reactions, and by the chemical environment in which this speciation process occurs. Some elements exist in several oxidation states simultaneously and form a number of individual species of widely differing chemical characteristics. Because such chemical and physical characteristics determine the ability of the species to be transported, the MINTEQ code is used in this methodology.

To apply the MINTEQ code, it was necessary to specify key solution parameters, including organic constituents, background ionic species, pH and Eh. Organic ligands that could solubilize metals were selected on the basis of data from studies of municipal landfill leachate. A total organic level of 15,000 mg/ℓ in raw leachate was utilized on the basis of the maximum organic levels measured in sludge landfill leachate (U.S. EPA, 1978). The total organic loading modeled consisted of six representative compounds for which required data on thermodynamics were available:

Acetate-1 (mol. wt. 59.05)
Glutamate-2 (mol. wt. 145.13)
Glycine-1 (mol. wt. 74.07)
Phthalate-2 (mol. wt. 164.13)
Salicylate-2 (mol. wt. 136.12)
Tartrate-2 (mol. wt. 148.09)

Since it was assumed that the leachate will not control groundwater chemistry, it was necessary to simulate dilution arising from mixing of the leachate into the aquifer. It was also assumed that only a portion of the total organic load in leachate represented ionic species capable of solubilizing metals. In recognition of both dilution and the identity of individual fractions of the total organic loading, it was estimated that 0.01 of the maximum level of organics observed in sludge monofill leachate (15,000 mg/ℓ) would be present as ionic organic ligands capable of solubilizing metals.

Given the 0.01 fraction selected, the organic ligands for the MINTEQ runs were entered in the following concentrations:

Acetate	11.99 mg/ℓ
Glutamate	29.46 mg/ℓ
Glycine	15.04 mg/ℓ
Phthalate	33.32 mg/ℓ
Salicylate	27.63 mg/ℓ
Tartrate	30.06 mg/ℓ
Total	147.5 mg/ℓ

Inorganic species and concentrations for the MINTEQ runs were selected on the basis of median values of national groundwater data included in the STORET system as presented in Table 4-3.

Six combinations of pH and Eh were selected for model runs: pH = 6.0 and 7.0; Eh = -200, +150 and +500 mv. The Eh values bracket those reported as typical for groundwater (Baas-Becking et al., 1960). The pH values address the lower half of the 6-8.5 range reported for groundwaters. These lower values are considered conservative because they are more likely to mobilize metals than pH levels of 7.5-8.5. Low pH and Eh values represent water affected by leachate where acid has been formed and oxygen is depleted.

For each contaminant of interest, a series of model runs were made introducing the contaminant at the concentrations listed in Table 4-4. Results of the model runs were then plotted showing the output concentrations as a function of input levels for each pH-Eh combination. These results are presented in Appendix B (Figures B-2 through B-6). Since each contaminant was modeled separately, no provision was made for interactions arising from multiple contaminants entering simultaneously.

To account for the geochemistry, the applicant need only determine the pH and Eh conditions of local groundwater and the level of contaminants in leachate. It is difficult to obtain accurate Eh measurements because the sample rapidly goes to a high oxidation level upon contact with air. However, because the more oxidized state yields higher metal mobility, the error introduced by poor sampling will essentially add a greater degree of safety. The appropriate graphs are selected from Appendix B (Figures B-2 through B-6) on the basis of having similar pH and Eh values. The leachate contaminant concentrations are then entered as inputs and the resulting

TABLE 4-3

Background Inorganic Constituents for MINTEQ Model Runs
(temperature: 14°C)

Chemical	Concentration (mg/ℓ)
Aluminum	0.200
Arsenic	0.010
Barium	0.200
Bicarbonate	190.000
Bromide	0.300
Cadmium	0.005
Calcium	48.000
Carbonate	0.000
Chloride	15.000
Chromium	0.202
Copper	0.020
Iron	0.200
Lead	0.010
Magnesium	14.000
Manganese	0.040
Mercury	0.0005
Nitrate	1.000
Phosphate	0.090
Selenium	0.005
Silver	0.010
Sulfate	25.000
Sulfide	0.200
Thallium	0.040

TABLE 4-4

Contaminant Concentrations Employed in Benchmark MINTEQ Runs

Contaminant (mg/ℓ)	Model Input Concentrations
Arsenic	0.06/1.25/2.5/5.0
Copper	1.32/32.5/65.4/130
Lead	0.03/0.5/1.0/2.0/10.0
Mercury	0.0035/0.075/0.15/0.30
Nickel	0.16/3.75/7.5/15

groundwater concentration identified from the curve as the starting point for subsequent saturated zone modeling.

To illustrate, assume an applicant has a predicted leachate concentration at the base of the unsaturated zone of 6 mg/ℓ and a site with groundwater at pH 7.2 and Eh 200 mv. The contaminant concentration in the groundwater (aquifer) would be determined by selecting the MINTEQ figure for this contaminant with the closest match for the pH and Eh conditions (pH of 7.0 and Eh of 150 mv) and reading the appropriate value. As illustrated in Figure 4-3, an input concentration of 6 mg/ℓ (abscissa value) yields an aquifer concentration of 1.0 mg/ℓ (ordinate value). This result would then be used for the input concentration (C_o) to the saturated zone model.

Nitrate is included in the MINTEQ data base. However, it was found that nitrate, like chlorides, was not solubility limited in any of the runs; therefore, no graph was constructed, and input levels to the saturated zone should be equated with output from the unsaturated zone.

The predicted inorganic contaminant concentrations in the saturated zone are compared to health criteria or effects thresholds. If they are less than the threshold, the contaminant is dropped from further consideration. If they exceed the threshold, they are input to the saturated zone transport model.

4.3.3.2. TRANSPORT CODE SELECTION CRITERIA -- The same criteria used to select a method for calculating travel time in the unsaturated zone are relevant for the saturated zone, namely the following: (1) the method should be appropriate for a wide range of applications, and (2) the data required by the method should be generally available. A more detailed discussion of these criteria is presented in Section 4.3.2.1.

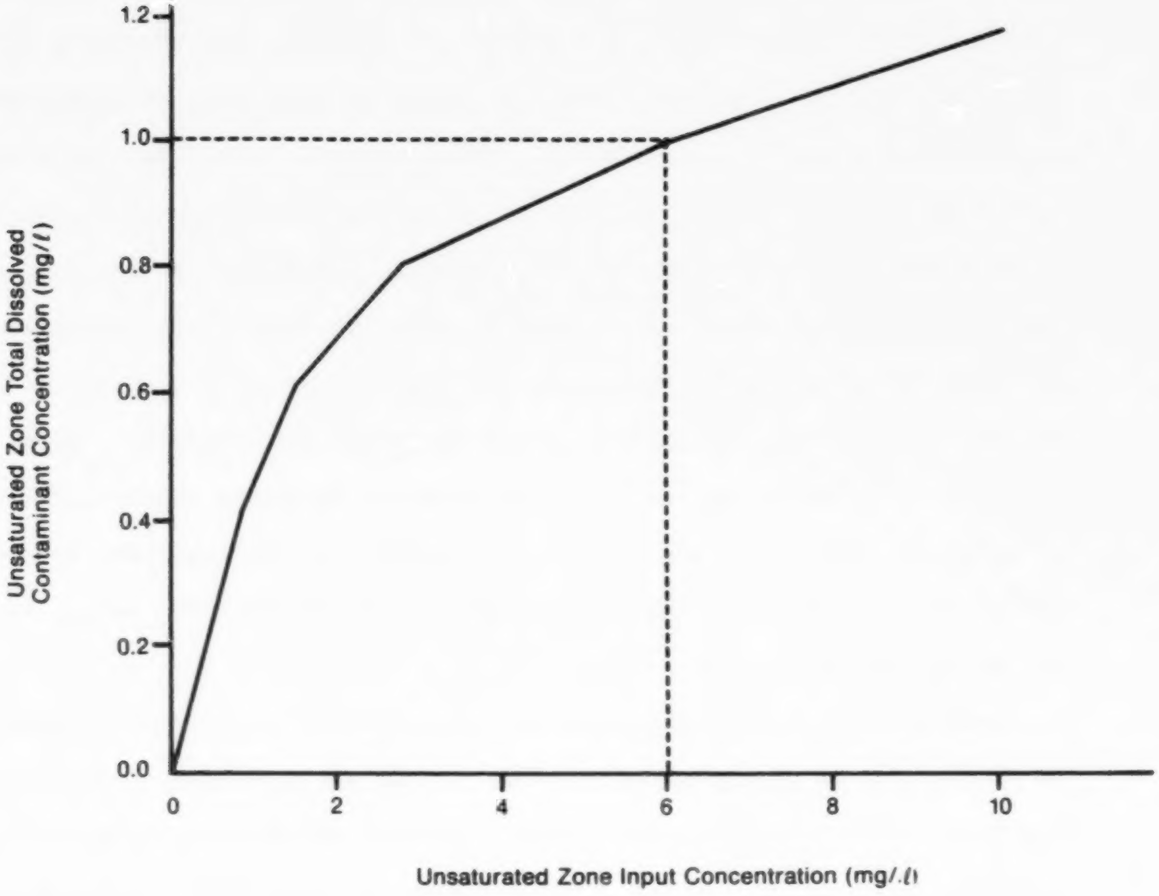


FIGURE 4-3

Example MINTEQ Speciation Results for Entry of a Contaminant into the Saturated Zone for Conditions of pH = 7.0 and Eh = 1.50 mv

4.3.3.3. TECHNICAL APPROACHES FOR DETERMINING TIME OF TRAVEL AND CONTAMINANT CONCENTRATION IN THE SATURATED GROUNDWATER FLOW SYSTEM -- There are two basic approaches to estimating contaminant travel time (velocity) and concentration in the saturated groundwater flow system: analytical solutions and numerical modeling. Analytical solutions are relatively quick and simple to use. However, they are based on a variety of simplifying assumptions related to contaminant characteristics and the subsurface environment. Consequently, the methods provide order-of-magnitude estimates of contaminant travel time and concentration. Numerical models, on the other hand, are far less restricted with regard to simplifying assumptions, but they typically require more data, are time consuming to set up and run, and require expensive and/or specialized equipment and expertise. Based on the above information and the selection criteria discussed earlier, the use of numerical models is not required. However, if the applicant believes that a more accurate portrayal of transport is worth the added costs, he or she may opt to employ such a model.

Numerous analytical methods/models for predicting contaminant transport/ concentrations in the groundwater flow system are available (Lapidus and Amundson, 1952; Davidson et al., 1968; Lindstrom and Boersma, 1971; Lai and Jurinak, 1972; Warrick et al., 1971; Cleary et al., 1973; Lindstrom and Stone, 1974; Marino, 1974; Kuo, 1976; Yeh and Tsai, 1976; Van Genuchten and Wierenga, 1976; Selim and Mansell, 1976; Wang et al., 1977; Yeh, 1981; Donigian et al., 1983). Most of these solutions/models are based on the advection-dispersion equation for predicting solute movement through porous media. The basic difference among them is their simplifying assumptions that make them specific to a particular problem.

4.3.3.4. ANALYTICAL METHODS/MODELS FOR ESTIMATING CONTAMINANT CONCENTRATIONS IN THE GROUNDWATER FLOW SYSTEM -- A number of analytical models are available for predicting saturated transport as presented in Table 4-5. Two of these analytical methods for estimating contaminant concentration in the saturated groundwater flow system are discussed here for illustrative purposes. In both cases, the methods are described in fairly general terms. References are provided for a detailed discussion of the methods and their application.

The first method is the analytical solution to the advective-dispersive equation. The second method describes the use of the AT123D analytical model (Yeh, 1981), which solves the advective-dispersive equation. It is coded such that it can be run on a personal computer, and it has the capability to handle many different types of boundary conditions.

The advective-dispersive equation forms the basis of all solution algorithms for predicting solute movement through saturated porous media. This equation assumes constant groundwater velocity (steady flow) in the longitudinal direction. It was developed for solving the limiting case of unidirectional advective transport with three-dimensional dispersion in a homogeneous and isotropic aquifer. Contaminant decay and retardation can be described by a first-order degradation rate and an equilibrium (partitioning or distribution) coefficient, respectively.

In three dimensionals with the average flow along the x axis, the advective-dispersive equation can be written as:

$$R \frac{\partial C}{\partial T} + \bar{V} \frac{\partial C}{\partial x} = D_{\ell} \frac{\partial^2 C}{\partial x^2} + D_{T\ell} \frac{\partial^2 C}{\partial y^2} + D_{Tv} \frac{\partial^2 C}{\partial z^2} - \lambda RC \qquad (4\text{-}20)$$

TABLE 4-5

Analytical Solutions of the Advective-Dispersive Equation

Author	Title
Boutwell, S.H S.M. Brown, B.R. Roberts and A.D. Atwood	Modeling Remedial Actions at Uncontrolled Hazardous Waste Sites. EPA/540/2-85-001. U.S. EPA, Cincinnati, OH. 1985.
Cleary, R.W. and M.J. Ungs	Analytical Models for Groundwater Pollution and Hydrology. Report 78-WR-15. Water Resources Program, Department of Civil Engineering, Princeton University, Princeton, NJ. 1978.
Codell, R.B.	Collection of Mathematical Models for Dispersion in Surface Water and Groundwater. NUREG-0868. Nuclear Regulatory Commission, Bethesda, MD. 1982.
Codell, R.B.	Simplified Analysis for Liquid Pathway Studies. NUREG-1054. Nuclear Regulatory Commission, Bethesda, MD. 1984.
Donigian, A.S. et al.	Rapid Assessment of Potential Groundwater Contamination Under Emergency Response Conditions. Anderson-Nichols & Co., Inc., Palo Alto, CA. EPA-68-3116. 1983.
Van Genuchten, M.T. and W.J. Alves	Analytical Solutions of the One-Dimensional Convective-Dispersive Solute Transport Equation. U.S. Dept. of Agriculture, Tech. Bull. No. 1661. 1982.
Yeh, G.T.	AT123D: Analytical Transient One-, Two-, and Three-Dimensional Simulation of Waste Transport in the Aquifer System. ORNL-5602. Environmental Sciences Div., Pub. No. 1439. Oak Ridge National Laboratory, Oak Ridge, TN. 1981.

where:

C = solution concentration (M/L^3)

D_ℓ, $D_{T\ell}$, D_{Tv} = longitudinal, lateral transverse and vertical transverse hydrodynamic dispersion coefficients (L^2/T)

$\bar{V}$ = average interstitial pore-water velocity in the x direction (L/T)

T = time (T)

x, y, z = Cartesian coordinates

λ = degradation/decay rate (T^{-1})

RF = retardation factor

Because the flow is unidirectional along the layering and is almost horizontal, the Cartesian coordinate axes are oriented in directions parallel to and normal (perpendicular) to the mean flow direction. The coefficients of hydrodynamic dispersion appearing in Equation 4-20 include both the effects of mechanical dispersion and molecular diffusion (D^*). They are of the form:

$$D_\ell = \alpha_\ell \bar{V} + D^* \tag{4-21a}$$

$$D_{T\ell} = \alpha_{T\ell} \bar{V} + D^* \tag{4-21b}$$

$$D_{Tv} = \alpha_{Tv} \bar{V} + D^* \tag{4-21c}$$

If the amount of spreading due to molecular diffusion is insignificant relative to the mixing caused by mechanical dispersion, then D^*, the molecular diffusion coefficient of a solute in porous medium, is generally ignored. Since this analysis focuses on a compliance point directly downflow from the source, dispersion will always exceed diffusion effects unless velocity approaches zero. In those cases, the dispersion coefficient is selected to encompass both effects. Unless site-specific information on dispersion is available, dispersion in the direction of flow may be assumed equal to one-tenth the distance to the point of compliance times the pore-water velocity (Donigian et al., 1983).

For a contaminant that travels with the groundwater, the average linear pore-water velocity can be calculated as:

$$\bar{V} = -\frac{K}{\theta}\frac{\partial H}{\partial x} \qquad (4\text{-}22)$$

where:

K = hydraulic conductivity of the medium (L/T)

$\frac{\partial H}{\partial x}$ = hydraulic gradient (dimensionless)

θ = effective porosity (dimensionless)

For contaminants that adsorb onto the soil matrix, the retardation factor must be estimated. The retardation factor (RF) is a measure of the mobility of the contaminant in the porous media. It represents the ratio of the mean pore-water velocity to the mean contaminant migration velocity and can be calculated as:

$$RF = 1 + (B/\theta)(Kd) \qquad (4\text{-}23)$$

where:

B = bulk density of the soil (kg/m^3)
θ = effective porosity (dimensionless)
Kd = distribution coefficient (ℓ/kg)

Values for effective porosity are provided in Appendix B.

The pollutant source is applied as continuous step functions of initial concentration (C_o) and duration (T_p) with the following boundary conditions:

$$C\ (x,o) = 0 \qquad (4\text{-}24a)$$

$$C\ (o,t) = C_o \qquad (4\text{-}24b)$$

$$\frac{dC}{dx}\ (\infty,t) = 0 \qquad (4\text{-}24c)$$

The analytical solution of the advective-dispersive equation (4-20), as given by Cho (1971), Misra et al. (1974), Van Genuchten and Alves (1982) and Rao (1982), can be expressed as:

$$\begin{aligned} C(x,t) &= C_o\ C^*(x,t) \text{ for } o < t \leq T_p \qquad (4\text{-}25) \\ &= C_o\ C^*(x,t) - C^*(x,\ t-T_p) \text{ for } t > T_p \end{aligned}$$

where $C^*(x,t)$ is given by

$$C^*(x,t) = \frac{1}{2} \left\{ \exp \frac{[(v-w)\ x]}{2D} \operatorname{erfc} \frac{[Rx\ -\ wt]}{2\sqrt{DRt}} + \exp \frac{[(v+w)\ x]}{2D} \operatorname{erfc} \frac{[Rx\ -\ wt]}{2\sqrt{DRt}} \right\}$$

and

$$w = (v^2 + 4\ DR\ \lambda)^{1/2}$$

(exp denotes the natural logarithm exponential and erfc the complementary error function.)

$$\operatorname{erfc}(z) = \int_z^{+w} \exp(-s^2)ds$$

as found tabulated in standard reference texts (i.e., Abramowitz and Stegun, 1972).

The boundary conditions shown in Equation 4-24(a,b,c) indicate that:

- No contaminant is present in the soil prior to input from the source.
- The input concentration at the surface is constant at C_0.
- A semi-infinite column is assumed with a zero-concentration gradient at the bottom. This last boundary condition is often assumed to allow development of the analytical solution; Van Genuchten and Alves (1982) indicate that this assumption has a relatively small influence on the accuracy of the solution in most circumstances when applied to well-defined finite systems.

The parameters required to solve the advective-dispersive equation, along with their symbols and recommended units, are listed in Table 4-6.

The second method for predicting the spatio-temporal distribution of contaminants in an aquifer is the AT123D code developed by Yeh (1981). This method is based on the basic advective-dispersive equation just discussed; however, it is coded in a format that makes it easy to use, and that allows for implementation of numerous options (450 in all). These options provide the code with the capability to simulate a wide variety of configurations and situations of source release and types of boundary conditions.

The data required to run the AT123D code are as follows:

- Geometry of the region of interest (x, y and z dimensions);
- Geometry of the source of contamination (xs, ys and zs dimensions);
- Dispersion coefficients in the x, y and z directions (D_x, D_y and D_z);
- Soil properties of effective porosity and bulk density (θ, B);
- Hydraulic conductivity (K);
- Source/sink strength (Q);

TABLE 4-6

Required Parameters for Solution of the Advective-Dispersive Equation*

Parameter/Boundary Condition	Symbol	Recommended Unit
Source concentration	C	mg/ℓ
Interstitial pore-water velocity	V	cm/day
Dispersion coefficient	D	cm^2/day
Degradation/decay rate parameter	λ	day^{-1}
Retardation factor (function of following characteristics)	$RF = 1 + \frac{BKd}{\theta}$	dimensionless
Distribution coefficient	Kd	mℓ/g
Soil bulk density	B	g/cm^3
Effective porosity	θ	dimensionless
Pulse duration (pulse input only)	t_0	day

*Source: Donigian et al., 1983

- o Distribution coefficient (soil-waste interaction parameter) (Kd);
- o Flow field (groundwater velocity) (V_x, V_y and V_z);
- o Decay constant (λ); and
- o Background concentrations of contaminants of interest;

A complete description of this code and its application is contained in Yeh (1981).

4.3.3.5. **CALCULATING STREAM CONCENTRATIONS RESULTING FROM GROUNDWATER SEEPAGE** -- A supplementary groundwater pathway is the exposure from edible aquatic organisms living in surface water recharged by contaminated groundwater. This pathway is assumed to be represented by the consumption of fish caught in a stream near a landfill. The concentration of the contaminant in the stream is first calculated under the conservative assumption that all of the contaminants exiting the unsaturated zone beneath the landfill seep into the stream:

$$\text{Stream Concentration} = C_{us} \times \frac{R \times A}{Q_f} \qquad (4\text{-}25a)$$

where:

C_{us} = contaminant concentration exiting the unsaturated zone
R = net recharge
A = landfill area
Q_f = stream flow

and the units are internally consistent.

The resulting stream concentration is then compared with the reference concentration in surface water (RWC), as described in the surface runoff chapter of the companion methodology document on land application and distribution and marketing of municipal sludge (U.S. EPA, 1989). The expressions in that document take into consideration bioconcentration factors, fish ingestion rate, water ingestion rate, etc.

As an example, if the values of:

$R = 0.5$ m/year

$A = 100$ m x 10 m = 1000 m^2

$Q_f = 1$ m^3/sec

are used to calculate the factor to convert leachate concentration to stream concentration, a dilution factor of 0.0000158 is obtained.

4.3.3.6. **ACCOUNTING FOR BACKGROUND CONTAMINANT CONCENTRATIONS IN THE GROUNDWATER** -- If background groundwater concentration levels for the contaminants of interest are measurable, these should be incorporated into the procedure by adding the background concentration to the final model-predicted concentration at the property boundary and comparing this total concentration to the health criteria.

4.3.4. Setting National Criteria. The methodology presented herein has been devised to evaluate municipal sludge landfill disposal on a site-specific basis. As mentioned previously, it can also be employed to establish sludge contaminant concentration criteria to be administered on a national or regional scale. For this purpose, the mode of operation is the reverse of that presented in earlier portions of this chapter. That is, the analysis begins with the selected health effects criteria and works backward to determine how high a concentration in the sludge could be before environmental levels would exceed that threshold. Hence, the analysis begins with the point of compliance, moves back through the aquifer to the point below the disposal facility and then moves up through the unsaturated zone to the disposal cell and the sludge itself.

Functionally, the reverse operation is not so straightforward. Some of the models and constructs employed in the methodology cannot be operated in the reverse mode, i.e., the analytical model is not closed form, so one cannot set the final concentration and solve for the initial concentration. Given constant dispersion and degradation, outflow concentration is a function of two factors -- leachate concentration and leach duration. Therefore, specifying an outflow concentration does not specify what the input parameters must be because many combinations of the input parameters can produce the same outflow concentration. Thus, it is necessary to make a series of forward calculations for a range of values and then work backward to obtain the national criteria levels.

Because the methodology is not reversible, the results of the national criteria calculation are not unique values of acceptable contaminant concentrations in the sludge. Instead, the result presented is a graph of a family of curves that relate the input leachate concentration (out of the landfill) to the groundwater concentration at the facility boundary. Each curve on the graph represents a certain pulse or release time. Given the health effects criteria concentration at the facility boundary and the initial pulse or release duration, the maximum acceptable input concentration can be obtained from the graph. From the input concentration, the total mass of contaminant in the sludge can then be calculated. This entire methodology will be discussed in more detail in the following text, and an example will be provided.

To develop the graph of the family curves, it is necessary to run the modeling sequence (unsaturated and saturated zone models) discussed previously for a range of pulse durations and contaminant input concentrations. The first step is to run the unsaturated zone transport model (CHAIN) using a range of pulse durations and contaminant (leachate) concentrations. Pulse durations of 1, 10, 100 and 1000 years and contaminant concentrations of 10, 100 and 1000 times the health effects criteria are recommended. All other input parameters to the model should be representative of the region being simulated, or in the case of national criteria, representative of the reasonable or probable worst case.

The results of the CHAIN model runs provide a series of release durations and peak concentrations for input to the saturated transport code (AT123D). The release duration obtained from the CHAIN results is defined as the period of time when the output concentration first reaches 1% of the peak concentration until the time after the peak declines to <1% of the peak. The peak concentration is used as the contaminant concentration during the entire release period and is a conservative assumption.

For the organics, the peak output concentration from CHAIN becomes the input concentration to AT123D. For the metals, the peak output concentration from CHAIN is adjusted using the appropriate MINTEQ curve in Appendix B (Figures B-2 through B-6) to predict the resulting concentration after geochemical reaction. This resulting concentration is used as the input concentration to AT123D.

The AT123D code requires a contaminant input flux rate that is the input concentration obtained from CHAIN or MINTEQ (Appendix B) times the surface recharge rate. The release times from CHAIN become the input pulse times to

AT123D. All other input parameters to AT123D shall be representative of the region or national case being simulated. The AT123D code is then run for this range of input concentrations and pulse times to predict a range of peak output concentrations.

At this point in the methodology the output consists of pairs of initial leachate concentration (X_i) (below the landfill) and peak output concentration (X_f) (at the property boundary) for each initial pulse duration simulated. These pairs can all be plotted on the same graph (X_f on the horizontal axis and X_i on the vertical axis) to yield a family of curves (one curve for each pulse duration). An example graph is shown in Figure 4-4.

The family of curves can be used as follows in working backward to determine a national criteria. Locate the point on a specific pulse time curve whose abscissa is equal to the health effects criteria value for the desired contaminant. The ordinate of this point is the maximum allowable leachate concentration in the landfill for pulse times equal to or less than the pulse time of the corresponding curve. A maximum allowable leachate concentration can be obtained from the graph for each pulse time curve.

The last step of the methodology is to calculate the total leachable mass (M_L) and the total mass (M) of contaminant in the landfill. For non-degradable contaminants, the total leachable mass can be calculated as the product of the initial leachate concentration (X_i) (as determined from the family of curves), times the recharge rate (R), times the pulse time (T_p):

$$M_L = X_i \, R \, T_p \tag{4-26}$$

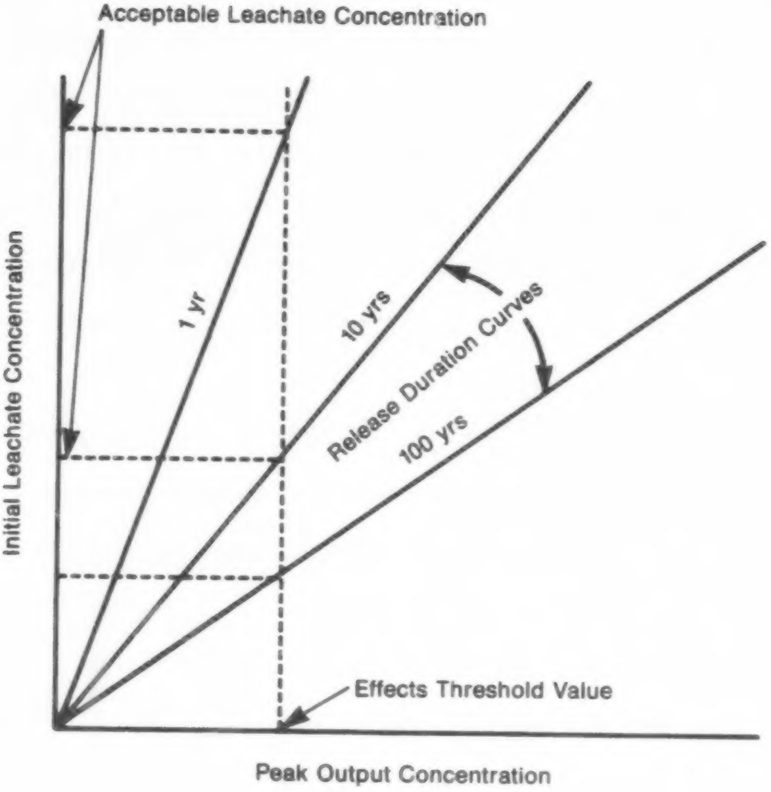


FIGURE 4-4

Example Graph of the Family of Curves Obtained for the National Criteria Case

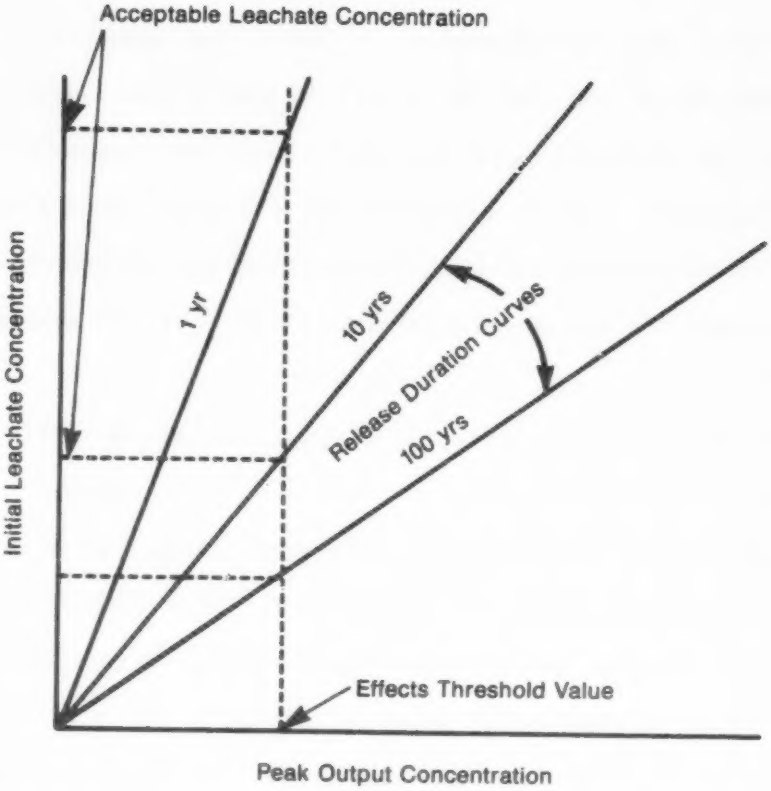


FIGURE 4-4

Example Graph of the Family of Curves Obtained for the National Criteria Case

For degradable contaminants, the degradation rate constant (λ) enters the calculations and the equation is:

$$M_L = \frac{X_i \ R \ (e^{\lambda T} \quad p-1)}{\lambda} \tag{4-27}$$

The total mass of contaminant in the sludge consists of that sorbed on the sludge solids and that dissolved in the sludge water. Therefore, the total mass of contaminant in the landfill for both degradable and nondegradable contaminants can be calculated as the total leachable mass plus the product of the initial leachate concentration (as determined from the family of curves) and the volume of water that drains from the sludge (D_V):

$$M = M_L + X_i \ D_V \tag{4-28}$$

There may exist a whole range of solutions for a particular simulation, so it is not possible to choose a unique result. However, from experience it appears that for many cases the methodology can be simplified and a somewhat unique solution can be obtained. This simplification is usually the result of the peak output concentration asymptotically reaching a maximum value as the pulse time increases, or as a result of solubility limits being realized in the saturated flow system. Examples of these processes are provided in the site-specific applications discussed in Section 4.5.

4.4. INPUT PARAMETER REQUIREMENTS

A number of inputs are required to apply the landfill alternative groundwater pathway review methodology to a specific site or proposed site. This section summarizes these inputs and provides information on where data may be obtained.

4.4.1. Fate and Transport: Pathway Data.

4.4.1.1. SOURCE TERM --

1. Sludge Moisture Content (L) -- Derived directly from gravi- metric analysis of sludge [ASTM Method G 51-77 (1984)].

2. Storage Capacity of Sludge (S) -- Derived gravimetrically as the moisture content of the sludge when completely drained by gravity [ASTM Method G 51-77 (1984)].

3. Net Recharge (R) -- Obtained from local weather station data or agricultural extension offices.

4.4.1.2. UNSATURATED ZONE --

1. Depth to Groundwater (hy) -- Determined from site plan and borings.

2. Distance from Landfill to Property Boundary (ds) -- Determined from site plan. Should equal the buffer strip width between the fill area and the property fence. Cannot exceed 150 m.

3. Stratigraphy -- Taken from site borings and/or local geological maps to determine the soil types and sequencing of the types.

4. Stratigraphic Layer Thickness -- Estimated from borings and/or local geological maps.

5. Saturated Soil Hydraulic Conductivity (K_{sat}) -- Measured in the field or laboratory [ASTM Method D2434-68 (1974)].

6. Slope of the Log-Log Plot of Air Entry Matrix Potential (ψe) and Field Moisture Content (f) for Soils (b) -- Derived experimentally or estimated from data presented in Appendix B (ASTM Method D2216-80).

7. Saturated Soil Moisture Content (fs) -- Derived experimentally or estimated from data presented in Appendix B (ASTM Method D2216-80).

8. Bulk Density of Soil (B) -- Derived experimentally or taken from the literature. A common value applied here is 1600 kg/m^3 (ASTM Method D2937-83).

4.4.1.3. SATURATED ZONE --

1. Groundwater pH -- Determined by direct measurement [ASTM Method G 51-77 (1984)].

2. Groundwater Eh -- Determined by direct measurement.

3. Hydraulic Conductivity in the Aquifer (K) -- Determined from field tests or taken from data presented in Appendix B.

4. Effective Porosity (θ_e) -- Determined directly or taken from data presented in Appendix B (ASTM Method D 4404-84).

5. Hydraulic Gradient ($\partial H/\partial x$) -- Determined from field data on potentiometric head (water table) or estimated from topography.

6. Bulk Density of Aquifer Media (B) -- Determined experimentally or taken from the literature. Typical value for soils is 1600 kg/m^3 (ASTM Method D 2937-83).

7. Dispersion Coefficient (Kd) -- Derived from the following:

$$D_x = 0.1 \left(\frac{\partial H}{\partial x}\right) \left(\frac{K}{\theta}\right) ds \tag{4-29a}$$

$$D_y, D_z = 0.01 \left(\frac{\partial H}{\partial x}\right) \left(\frac{K}{\theta}\right) ds \tag{4-29b}$$

8. Geometry of the Site -- Taken from site maps.

4.4.2. Fate and Transport: Chemical-Specific Data.

4.4.2.1. SOURCE TERM --

1. Contaminant Concentration in Sludge (N) -- Derived directly for each contaminant by analyzing a sample of the sludge using an approved digestion technique.

2. Contaminant Concentration in Leachate (X) -- Derived directly for each contaminant by applying the partition coefficient to the total sludge concentration for organic contaminants and maximum solubility levels for inorganic constituents.

4.4.2.2. UNSATURATED ZONE --

1. Unsaturated Zone Distribution Coefficient (Kd) -- In Tier 2, the Kd value is derived experimentally.

2. Unsaturated Zone Degradation Rate Constant (λ_u) -- Selected values from the literature are provided.

4.4.2.3. SATURATED ZONE --

1. Saturated Zone Distribution Coefficient (Kd) -- Selected from Appendix B.

2. Saturated Zone Degradation Constant (λ_s) -- Values provided as taken from the scientific literature.

4.4.3. Health Effects Data. A reference water concentration (RWC, in mg/ℓ) will be defined as a groundwater concentration used to evaluate the potential for adverse effects on human health as a result of sludge landfilling. That is, for a given landfill site, and given the practice definitions and assumptions stated previously in this methodology, the criterion for a given sludge contaminant is the concentration in the sludge that cannot be exceeded, and is calculated to result in groundwater concentrations below the RWC at the well site. Exceeding the RWC would be a basis for concern that adverse health effects may occur in a human population in the site vicinity.

RWC is determined based upon contaminant toxicity and water ingestion rate, from the following general equation:

$$\text{Reference Water Concentration: } RWC = I_p / I_w \qquad (4\text{-}30)$$

where I_p is the acceptable chronic pollutant intake rate (in mg/day) based on the potential for health effects, and I_w is the water ingestion rate (in ℓ/day). This simplified equation assumes that the ingested contaminant is absorbed into the body via the gastrointestinal tract at the same rate in humans as in the experimental species tested, or between routes of exposure (e.g., oral and inhalation). Also, this equation assumes that there are no other exposures of the contaminant from other sources, natural or manmade. I_p varies according to the pollutant evaluated and to whether the pollutant acts according to a threshold or nonthreshold mechanism of toxicity.

4.4.3.1. **THRESHOLD-ACTING TOXICANTS** -- Threshold effects are those for which a safe (i.e., subthreshold) level of toxicant exposure can be estimated. For these toxicants, RWC is derived as follows:

$$\text{Reference Water Concentration: } RWC = \left[\left(\frac{RfD \times bw}{RE}\right) - TBI\right] \div I_w \qquad (4\text{-}31)$$

where:

RfD = reference dose (mg/kg/day)

bw = human body weight (kg)

TBI = total background intake rate of pollutant from all other sources of exposure (mg/day)

I_w = water ingestion rate (ℓ/day)

RE = relative effectiveness of exposure (unitless)

The definition and derivation of each of the parameters used to estimate RWC for threshold-acting toxicants are further discussed below.

4.4.3.1.1. Reference Dose (RfD) -- When toxicant exposure is by ingestion, the threshold assumption has traditionally been used to establish an acceptable daily intake, or ADI. The Food and Agricultural Organization and the World Health Organization have defined ADI as "the daily intake of a chemical which, during an entire lifetime, appears to be without appreciable risk on the basis of all the known facts at the time. It is expressed in milligrams of the chemical per kilogram of body weight (mg/kg)" (Lu, 1983). Procedures for estimating the ADI from various types of toxicological data were outlined by the U.S. EPA in 1980 (Federal Register, 1980). More recently the Agency has preferred the use of a new term, the reference dose, or RfD, to avoid the connotation of acceptability, which is often controversial.

The RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of the daily exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious effects during a lifetime. The RfD is expressed in units of mg/kg bw/day. The RfD is estimated from observations in humans whenever

Reference Water Concentration: $$RWC = \left[\left(\frac{RfD \times bw}{RE}\right) - TBI\right] \div I_w \qquad (4\text{-}31)$$

where:

RfD = reference dose (mg/kg/day)

bw = human body weight (kg)

TBI = total background intake rate of pollutant from all other sources of exposure (mg/day)

I_w = water ingestion rate (ℓ/day)

RE = relative effectiveness of exposure (unitless)

The definition and derivation of each of the parameters used to estimate RWC for threshold-acting toxicants are further discussed below.

4.4.3.1.1. Reference Dose (RfD) -- When toxicant exposure is by ingestion, the threshold assumption has traditionally been used to establish an acceptable daily intake, or ADI. The Food and Agricultural Organization and the World Health Organization have defined ADI as "the daily intake of a chemical which, during an entire lifetime, appears to be without appreciable risk on the basis of all the known facts at the time. It is expressed in milligrams of the chemical per kilogram of body weight (mg/kg)" (Lu, 1983). Procedures for estimating the ADI from various types of toxicological data were outlined by the U.S. EPA in 1980 (Federal Register, 1980). More recently the Agency has preferred the use of a new term, the reference dose, or RfD, to avoid the connotation of acceptability, which is often controversial.

The RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of the daily exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious effects during a lifetime. The RfD is expressed in units of mg/kg bw/day. The RfD is estimated from observations in humans whenever possible. When human data are lacking, observations in animals are used, employing uncertainty factors as specified by existing Agency methodology.

RfD values for noncarcinogenic (or systemic) toxicity have been derived by several groups within the Agency. An Intra-Agency Work Group verifies each RfD, which is then loaded onto the Agency's publically available Integrated Risk Information System (IRIS) database. Most of the noncarcinogenic chemicals that are presently candidates for sludge criteria for the landfill pathway are included on the Agency's RfD list, and thus no new effort will be required to establish RfDs for deriving sludge criteria. For any chemicals not so listed, RfD values should be derived according to established Agency procedures (U.S. EPA, 1988).

4.4.3.1.2. Human Body Weight (bw) and Water Ingestion Rate (I_w) -- Both bw and I_w vary widely among individuals according to age and sex. Variations of mean drinking-water intake and body weight with age and sex for the U.S. population are illustrated in Table 4-7. The choice of values for use in risk assessment depends on the definition of the individual at risk, which in turn depends on exposure and susceptibility to adverse effects. The RfD (or ADI) was defined before as the dose on a body-weight basis that could be safely tolerated over a lifetime. As shown in Table 4-7, water consumption on a body-weight basis is substantially higher for infants and toddlers than for teenagers or adults. Therefore, infants and toddlers would be at greater risk of exceeding an RfD when exposure is by drinking water. However, the effects on which the RfD is based may occur after a long cumulative exposure period, in some instances approaching the

TABLE 4-7

Water Ingestion and Body Weight by Age-Sex Group in the United States

Age-Sex Group	Mean Water Ingestion[a] (mℓ/day)	Median Body Weight (kg)	Water Ingestion per Unit Body Weight[d] (mℓ/kg/day)
6-11 months	308	8.8[b]	35.1
2 years	436	13.5[b]	32.2
14-16 years, female	587	51.3[b]	11.4
14-16 years, male	732	54.2[b]	13.5
25-30 years, female	896	58.5[c]	15.3
25-30 years, male	1050	67.6[c]	15.5
60-65 years, female	1157	67.6[c]	17.1
60-65 years, male	1232	73.9[c]	16.7

[a] Source: Pennington, 1983. From the revised FDA Total Diet Study. Includes categories 193, 195-197, 201-203.

[b] Source: Nelson, 1969, as cited in Bogert et al., 1973. Calculated by averaging several age or sex groups.

[c] Source: Society of Actuaries, 1959, as cited in Bogert et al., 1973. Average body weights for median heights of 156 cm (5 ft, 5 in) and 173 cm (5 ft, 8 in) for females and males, respectively.

[d] The water ingestion/body-weight ratios have been derived from the referenced values for illustrative purposes only.

human lifespan. In these cases it may be reasonable to base the derivation of criteria upon adult values of bw and I_w. In cases where effects have a shorter latency (e.g., <10 years) and where children are known to be at special risk, it may be more appropriate to use values for toddlers or infants.

The approach presently employed in the derivation of recommended maximum contaminant levels (RMCLs) by the U.S. EPA Office of Drinking Water is to assume a bw and I_w of 70 kg and 2.0 ℓ/day, respectively (Federal Register, 1985), for adults and a bw and I_w of 10 kg and 1.0 ℓ/day, respectively, for a child.

4.4.3.1.3. Total Background Intake Rate of Pollutant (TBI) -- It is important to recognize that sources of exposure other than sludge disposal practices may exist, and that the total exposure should be maintained below the RfD. Other sources of exposure include background levels (whether natural or anthropogenic) in drinking water (other than groundwater), food or air. Other types of exposure, due to occupation or habits such as smoking, might also be included depending on data availability and regulatory policy. These exposures are summed to estimate TBI.

Data for estimating background exposure usually are derived from analytical surveys of surface, ground or tap water, from FDA market-basket surveys and from air-monitoring surveys. These surveys may report means, medians, percentiles or ranges, as well as detection limits. Estimates of TBI may be based on values representing central tendency or on upper-bound exposure situations, depending on regulatory policy. Data chosen to estimate TBI should be consistent with the value of bw. Where background data are reported in terms of a concentration in air or water, ingestion or inhalation rates applicable to adults or children can be used to estimate the proper daily background intake value. Where data are reported as total daily dietary intake for adults and similar values for children are unavailable, conversion to an intake for children may be required. Such a conversion could be estimated on the basis of relative total food intake or relative total caloric intake between adults and children.

As stated in the beginning of this subsection, the TBI is the summed estimate of all possible background exposures, except exposures resulting from a sludge disposal practice. To be more exact, the TBI should be a summed total of all toxicologically effective intakes from all nonsludge exposures. To determine the effective TBI, background intake values (BI) for each exposure route must be divided by that route's particular relative effectiveness (RE) factor. Thus, the TBI can be mathematically derived after all the background exposures have been determined, using the following equation:

$$\text{TBI} = \frac{\text{BI (food)}}{\text{RE (food)}} + \frac{\text{BI (nonsludge-derived water)}}{\text{RE (water)}} + \frac{\text{BI (air)}}{\text{RE (air)}} + \ldots + \frac{\text{BI (n)}}{\text{RE (n)}} \tag{4-32}$$

where:

TBI = total background intake rate of pollutant from all other sources of exposure (mg/day)

BI = background intake of pollutant from a given exposure route, indicated by subscript (mg/day)

RE = relative effectiveness of the exposure route indicated by subscript (unitless)

4.4.3.1.4. Fraction of Ingested Water From Contaminated Source -- It is recognized that an individual exposed to contaminated groundwater from a landfill may not necessarily remain in the landfill proximity for 24 hours/

day. However, if it is assumed that residential areas may be contaminated, it is likely that less mobile individuals will include those at greatest risk. Therefore, it is reasonable to assume that 100% of the water ingested by the MEIs will be from the area of the landfill.

4.4.3.1.5. Relative Effectiveness of Exposure (RE) -- RE is a unitless factor that shows the relative toxicological effectiveness of an exposure by a given route when compared to another route. The value of RE may reflect observed or estimated differences in absorption between the inhalation and ingestion routes, which can then significantly influence the quantity of a chemical that reaches a particular target tissue, the length of time it takes to get there, and the degree and duration of the effect. The RE factor may also reflect differences in the occurrence of critical toxicological effects at the portal of entry. For example, carbon tetrachloride and chloroform were estimated to be 40% and 65% as effective, respectively, by inhalation as by ingestion based on high-dose absorption differences (U.S. EPA, 1984b,c). In addition to route differences, RE can also reflect differences in bioavailability due to the exposure matrix. For example, absorption of nickel ingested in water has been estimated to be 5 times that of nickel ingested in the diet (U.S. EPA, 1985d). The presence of food in the gastrointestinal tract may delay absorption and reduce the availability of orally administered compounds, as demonstrated for halocarbons (NRC, 1986).

Physiologically based pharmacokinetic (PB-PK) models have evolved into particularly useful tools for predicting disposition differences due to exposure route differences. Their use is predicated on the premise that an effective (target-tissue) dose achieved by one route in a particular species is expected to be equally effective when achieved by another exposure route or in some other species. For example, the proper measure of target-tissue dose for a chemical with pharmacologic activity would be the tissue concentration divided by some measure of the receptor binding constant for that chemical. Such models account for fundamental physiologic and biochemical parameters such as blood flows, ventilatory parameters, metabolic capacities and renal clearance, tailored by the physicochemical and biochemical properties of the agent in question. The behavior of a substance administered by a different exposure route can be determined by adding equations that describe the nature of the new input function. Similarly, since known physiologic parameters are used, different species (e.g., humans vs. test species) can be modeled by replacing the appropriate constants. It should be emphasized that PB-PK models must be used in conjunction with toxicity and mechanistic studies in order to relate the effective dose associated with a certain level of risk for the test species and conditions to other scenarios. A detailed approach for the application of PB-PK models for derivation of the RE factor is beyond the scope of this document, but the reader is referred to the comprehensive discussion in NRC (1986). Other useful discussions on considerations necessary when extrapolating route to route are found in Pepelko and Withey (1985) and Clewell and Andersen (1985).

Since exposure for the groundwater pathway is by drinking water, the RE factors applied are all with respect to the drinking-water route. Therefore, the value of RE in Equation 4-31 gives the relative effectiveness of the exposure route and matrix on which the RfD was based when compared to drinking water. Similarly, the RE factors in Equation 4-32 show the relative effectiveness, with respect to the drinking-water route, of each background exposure route and matrix.

An RE factor should only be applied where well-documented, referenced information is available on the contaminant's observed relative effectiveness or its pharmacokinetics. When such information is not available, RE is equal to 1.

4.4.3.2. **CARCINOGENS** -- For carcinogenic chemicals, the Agency considers the excess risk of cancer to be linearly related to dose, except at high-dose levels (U.S. EPA, 1986a). The threshold assumption, therefore, does not hold, as risk diminishes with dose but does not become zero or background until dose becomes zero.

The decision whether to treat a chemical as a threshold- or nonthreshold-acting (i.e., carcinogenic) agent depends on the weight of the evidence that it may be carcinogenic to humans. Methods for classifying chemicals as to their weight of evidence have been described by U.S. EPA (1986a), and most of the chemicals that presently are candidates for sludge criteria have recently been classified in Health Assessment Documents or other reports prepared by the U.S. EPA's Office of Health and Environmental Assessment (OHEA), or in connection with the development of RMCLs for drinking-water contaminants (U.S. EPA, 1985e). To derive values of RWC, a decision must be made as to which classifications constitute sufficient evidence for basing a quantitative risk assessment on a presumption of carcinogenicity. Chemicals in classifications A and B, "human carcinogen" and "probable human carcinogen," respectively, have usually been assessed as carcinogens, whereas those in classifications D and E, "not classifiable as to human carcinogenicity because of inadequate human and animal data" and "evidence of noncarcinogenicity for humans," respectively, have usually been assessed according to threshold effects. Chemicals classified as C, "possible human carcinogen," have received varying treatment. For example, lindane, classified by the Human Health Assessment Group (HHAG) of the U.S. EPA as B2-C, or between the lower range of the B category and category C, has been assessed both using the linear model for tumorigenic effects (U.S. EPA, 1980b) and based on threshold effects (U.S. EPA, 1985e). Table 4-8 gives an illustration of these U.S. EPA classifications based on the available weight of evidence.

The use of the weight-of-evidence classification, without noting the explanatory material for a specific chemical, may lead to a flawed conclusion because some of the classifications are exposure-route dependent. Certain compounds (e.g., nickel) have been shown to be carcinogenic by the inhalation route but not by ingestion. The issue of whether or not to treat an agent as carcinogenic by ingestion remains controversial for several chemicals.

If a pollutant is to be assessed according to nonthreshold, carcinogenic effects, the RWC is derived as follows:

$$\text{Reference Water Concentration: } RWC = \left[\left(\frac{RL \times bw}{q_1^* \times RE}\right) - TBI\right] \div I_w \quad (4\text{-}33)$$

where:

q_1^* = human cancer potency [$(\text{mg/kg/day})^{-1}$]

RL = risk level (unitless) (e.g., 10^{-5}, 10^{-6}, etc.)

bw = human body weight (kg)

RE = relative effectiveness of exposure (unitless)

I_w = water ingestion rate (ℓ/day)

TBI = total background intake rate of pollutant (mg/day); from all other sources of exposure

TABLE 4-8

Illustrative Categorization of Evidence Based on Animal and Human Data*

Human Evidence	Animal Evidence				
	Sufficient	Limited	Inadequate	No Data	No Evidence
Sufficient	A	A	A	A	A
Limited	B1	B1	B1	B1	B1
Inadequate	B2	C	D	D	D
No data	B2	C	D	D	E
No evidence	B2	C	D	D	E

*The above assignments are presented for illustrative purposes. There may be nuances in the classification of both animal and human data indicating that different categorizations than those given in the table should be assigned. Furthermore, these assignments are tentative and may be modified by ancillary evidence. In this regard all relevant information should be evaluated to determine if the designation of the overall weight of evidence needs to be modified. Relevant factors to be included along with the tumor data from human and animal studies include structure-activity relationships; short-term test findings; results of appropriate physiological, biochemical and toxicological observations; and comparative metabolism and pharmacokinetic studies. The nature of these findings may cause an adjustment of the overall categorization of the weight of evidence.

The RWC, in the case of carcinogens, is thought to be protective because the q_1^* is typically an upper-limit value (i.e., the true potency is considered unlikely to be greater and may be less). The definition and derivation of each of the parameters used to estimate RWC for carcinogens are further discussed in the following subsections.

4.4.3.2.1. Human Cancer Potency (q_1^*) -- For most carcinogenic chemicals, the linearized multistage model is recommended for estimating human cancer potency from animal data (U.S. EPA, 1986a). When epidemiological data are available, potency is estimated based on the observed relative risk in exposed vs. nonexposed individuals, and on the magnitude of exposure. Guidelines for use of these procedures have been presented in the U.S. EPA (1980c, 1985e) and in each of a series of Health Assessment Documents prepared by OHEA (for example, U.S. EPA, 1985c). The true potency value is considered unlikely to be above the upper-bound estimate of the slope of the dose-response curve in the low-dose range, and it is expressed in terms of risk/dose, where dose is in units of mg/kg/day. Thus, q_1^* has units of $(mg/kg/day)^{-1}$. OHEA has derived potency estimates for each of the potentially carcinogenic chemicals that are presently candidates for sludge criteria. Therefore, no new effort will be required to develop potency estimates to derive sludge criteria.

4.4.3.2.2. Risk Level (RL) -- Since by definition no "safe" level exists for exposure to nonthreshold agents, values of RWC are calculated to reflect various levels of cancer risk. If RL is set at zero, then RWC will be zero. If RL is set at 10^{-6}, RWC will be the concentration which, for lifetime exposure, is calculated to have an upper-bound cancer risk of one case in one million individuals exposed. This risk level refers to excess cancer risk, i.e., over and above the background cancer risk in unexposed individuals. By varying RL, RWC may be calculated for any level of risk in the low-dose region, i.e., RL $\leq 10^{-2}$. Specification of a given risk level on which to base regulations is a matter of policy. Therefore, it is common practice to derive criteria representing several levels of risk without specifying any level as "acceptable."

4.4.3.2.3. **Human Body Weight (bw) and Water Ingestion Rate (I_w)** -- As with toxicants, it is important to gear the selection of bw and I_w to the nature of the effect of concern. Carcinogenesis normally has a long latency period and, therefore, adult values of bw and I_w have usually been applied. For example, the HHAG assumes 70 kg and 2 ℓ/day, respectively, to derive unit risk estimates for drinking water, which are potency estimates transformed to units of $(\mu g/\ell)^{-1}$. In addition, although exposure is somewhat higher in children when expressed on a body-weight basis (see Table 4-8), water ingestion occurs lifelong and groundwater concentrations tend to change only very slowly.

4.4.3.2.4. **Relative Effectiveness of Exposure (RE)** -- RE is a unitless factor that shows the relative toxicological effectiveness of an exposure by a given route compared to another route. The value of RE may reflect observed or estimated differences in absorption between the inhalation and ingestion routes, which can significantly influence the quantity of a chemical that reaches a particular target tissue, the length of time it takes to get there, and the degree and duration of the effect. The RE factor may also reflect differences in the occurrence of critical toxicological effects at the portal of entry. For example, carbon tetrachloride and chloroform were estimated to be 40% and 65% as effective, respectively, by inhalation as by ingestion based on high-dose absorption differences (U.S. EPA, 1984b,c). In addition to route differences, RE can also reflect differences in bioavailability due to the exposure matrix. For example, absorption of nickel ingested in water has been estimated to be 5 times that of nickel ingested in food (U.S. EPA, 1985d). The presence of food in the gastrointestinal tract may delay absorption and reduce the availability of orally administered compounds, as demonstrated for halocarbons (NRC, 1986).

PB-PK models have evolved into particularly useful tools for predicting disposition differences due to exposure route differences. Their use is predicated on the premise that an effective (target-tissue) dose achieved by one route in a particular species is expected to be equally effective when achieved by another exposure route or in some other species. For example, the proper measure of target-tissue dose for a chemical with pharmacologic activity would be the tissue concentration divided by some measure of the receptor binding constant for that chemical. Such models account for fundamental physiologic and biochemical parameters such as blood flows, ventilatory parameters, metabolic capacities and renal clearance, tailored by the physicochemical and biochemical properties of the agent in question. The behavior of a substance administered by a different exposure route can be determined by adding equations that describe the nature of the new input function. Similarly, since known physiologic parameters are used, different species (e.g., humans vs. test species) can be modeled by replacing the appropriate constants. It should be emphasized that PB-PK models must be used in conjunction with toxicity and mechanistic studies in order to relate the effective dose associated with a certain level of risk for the test species and conditions to other scenarios. A detailed approach for the application of PB-PK models for derivation of the RE factor is beyond the scope of this document, but the reader is referred to the comprehensive discussion in NRC (1986). Other useful discussions on considerations necessary when extrapolating route to route are found in Pepelko and Withey (1985) and Clewell and Andersen (1985).

Since exposure for the groundwater pathway is by drinking water, the RE factors applied are all with respect to the drinking-water route. Therefore, the value of RE in Equation 4-33 gives the relative effectiveness of the exposure route and the matrix on which the q_1* was based when compared to drinking water. Similarly, the RE factors in Equation 4-32 show the relative effectiveness, with respect to the drinking-water route, of each background exposure route and matrix.

An RE factor should only be applied where well-documented, referenced information is available on the contaminant's relative effectiveness or its pharmacokinetics. When such information is not available, RE is equal to 1.

4.4.3.2.5. Total Background Intake Rate of Pollutant (TBI) -- It is important to recognize that sources of exposure other than sludge disposal practices may exist, and that the total exposure should be maintained below the determined cancer risk-specific exposure level. Other sources of exposure include background levels (whether natural or anthropogenic) in drinking water (other than groundwater), food or air. Other types of exposure, due to occupation or habits such as smoking, might also be included depending on data availability and regulatory policy. These exposures are summed to estimate TBI.

Data for estimating background exposure usually are derived from analytical surveys of surface, ground or tap water, from FDA market-basket surveys and from air-monitoring surveys. These surveys may report means, medians, percentiles or ranges, as well as detection limits. Estimates of TBI may be based on values representing central tendency or on upper-bound exposure situations, depending on regulatory policy. Data chosen to estimate TBI should be consistent with the value of bw. Where background data are reported in terms of a concentration in air or water, ingestion or inhalation rates applicable to adults can be used to estimate the proper daily background intake value.

As stated in the beginning of this subsection, the TBI is the summed estimate of all possible background exposures, except exposures resulting from a sludge disposal practice. To be more exact, the TBI should be a summed total of all toxicologically effective intakes from all nonsludge exposures. To determine the effective TBI, background intake values (BI) for each exposure route must be divided by that route's particular relative effectiveness (RE) factor. Thus, the TBI can be mathematically derived after all the background exposures have been determined, using the following equation:

$$\mathrm{TBI} = \frac{\mathrm{BI\ (food)}}{\mathrm{RE\ (food)}} + \frac{\mathrm{BI\ (nonsludge\text{-}derived\ water)}}{\mathrm{RE\ (water)}} + \frac{\mathrm{BI\ (air)}}{\mathrm{RE\ (air)}} + \ldots + \frac{\mathrm{BI\ (n)}}{\mathrm{RE\ (n)}} \tag{4-32}$$

where:

TBI = total background intake rate of pollutant from all other sources of exposure (mg/day)

BI = background intake of pollutant from a given exposure route, indicated by subscript (mg/day)

RE = relative effectiveness, with respect to drinking-water exposure, of the exposure route indicated by subscript (unitless)

4.4.3.2.6. Fraction of Ingested Water From Contaminated Source -- It is recognized that an individual exposed to contaminated groundwater from a landfill may not necessarily remain in the landfill proximity for 24 hours/day. However, if it is assumed that residential areas may be contaminated, it is likely that less mobile individuals will include those at greatest risk. Therefore, it is reasonable to assume that 100% of the water ingested by the MEIs will be from the area of the landfill.

For volatile contaminants, the estimated intake from inhalation is converted to an equivalent ingestion dose in drinking water, which is added to the background concentration in groundwater. This accounts for intake of these contaminants via both routes simultaneously. Atmospheric concentrations are calculated in $\mu g/m^3$ and converted to equivalent drinking water concentrations in mg/ℓ by assuming an individual breathes 20 m^3 of air per day and drinks 2 ℓ of water. Therefore, 1 $\mu g/m^3$ of air results in a total intake of 20 μg from the air, being equivalent to drinking 2 ℓ of 10 μg/ℓ or 0.01 mg/ℓ water. Therefore, atmospheric concentrations in micrograms/cubic meter are multiplied by 0.01 to convert them to equivalent liquid concentrations before adding them to the composite aquifer concentration (leachate from the landfill plus background).

4.5. EXAMPLE CALCULATIONS

The methodology presented in the previous section can best be illustrated with an example calculation. In the following, calculations are first made for an individual site as would be the case with a site-specific application. Then an example is given for development of criteria for maximum allowable contaminant levels in sludge. To illustrate the methodology, the example considers an organic contaminant. Input parameters for the example calculations are provided in Table 4-9.

4.5.1. Site-Specific Application. A step-by-step discussion of a site-specific application follows. The application uses benzene as the constituent of interest. The input data are reiterated on the first pages of the application.

The reference water concentration (RWC) for the carcinogen benzene is derived using Equation 4-33:

$$RWC = \left[\left(\frac{RL \times bw}{q_1^* \times RE}\right) - TBI\right] \div I_w \qquad (4\text{-}33)$$

The risk level (RL), the body weight (bw) and the daily ingestion rate (I_w) are set for this example at 10^{-6}, 70 kg and 2 ℓ, respectively. The relative effectiveness factor (RE) is set at 1. The human cancer potency for benzene has been determined by the U.S. EPA to be 5.2×10^{-2} $(mg/kg/day)^{-1}$. Current total background intake (TBI) of benzene from all other sources, except from landfilling of sludges, has not been determined for 1986, but for illustrative purposes a TBI of zero is used here to derive an example RWC. Determination of an RWC for a specific landfill site should be based on a current local assessment of TBI.

$$RWC = \left[\left(\frac{10^{-6} \quad \times 70\ kg}{5.2 \times 10^{-2}\ (mg/kg/day)^{-1}}\right) - 0\right] \div (2\ \ell)$$

$$= 6.73 \times 10^{-4}\ mg/\ell$$

$$= 0.673\ \mu g/\ell$$

TABLE 4-9

Input Parameters for Example Calculations -- Groundwater

Fate and Transport: Pathway Data		
Source Term		
1.	Water content of sludge	$WS = 0.95$ kg/kg
2.	Storage capacity of sludge	$S = 0.90$ kg/kg
3.	Density of sludge	$D_s = 1012$ kg/m^3
4.	Net recharge	$R = 0.5$ m/year
Unsaturated Zone		
5.	Depth to groundwater	$hy = 1$ m
6.	Distance to property boundary	$ds = 100$ m
7.	Material	Sandy loam
8.	Thickness	$m = 1$ m
9.	Saturated soil hydraulic conductivity	$k_{sat} = 10^4$ m/year
10.	Slope of matric potential and moisture content plot	$b = 4.0$
11.	Saturated soil moisture content	$f_s = 0.39$ m^3/m^3
12.	Bulk density	$B_u = 1400$ kg/m^3
Saturated Zone		
13.	Groundwater	$pH = 6$
14.	Groundwater	$Eh = 150$ mv
15.	Hydraulic conductivity	$K = 1.5 \times 10^5$ m/yr
16.	Effective porosity	$\theta_e = 0.10$
17.	Hydraulic gradient	$(\partial H/\partial X) = 0.003$

TABLE 4-9 (cont.)

Fate and Transport: Pathway Data -- Saturated Zone (cont.)		
18.	Bulk density	B_S = 2390 kg/m^3
19.	Dispersion coefficient	D_x = 4.5x10^4 m^2/year D_y = 4.5x10^3 m^2/year D_z = 4.5x10^3 m^2/year
20.	Site geometry	
	Landfill width	SW = 10 m
	Landfill length	SL = 100 m
	Fill height	FH = 3.46 m
Fate and Transport: Chemical-Specific Data		
Source Term		
21.	Benzene	Concentration in leachate (X) = 0.05 mg/ℓ
22.	Benzene	Concentration in sludge (N) = 3 mg/kg
Unsaturated Zone		
23.	Benzene	Distribution coefficient (Kd) = 7.4x10^{-3} ℓ/kg
24.	Benzene	Degradation rate constant (λ) = 3.9 year^{-1}
Saturated Zone		
25.	Benzene	Distribution coefficient (Kd) = 0.0 ℓ/kg
26.	Benzene	Degradation rate constant (λ) = 0.0 year^{-1}
Chemical-Specific Data -- Health or Environmental Effects		
27.	Benzene	Reference water concentration (RWC) = 0.000673 mg/ℓ

4.5.1.1. TIER 1 -- Compare the concentration of each contaminant in the leachate (X) to the RWC.

	X (mg/ℓ)	RWC (mg/ℓ)
Benzene	0.05	0.000673

Continue with Tier 2 only if X exceeds RWC, which, in this case, is true for benzene.

4.5.1.2. TIER 2 -- Since benzene did not pass Tier 1, a Tier 2 analysis is required. The procedure that would be followed in a Tier 2 analysis is presented below in a step-by-step fashion.

4.5.1.2.1. Sludge/Landfill Calculations --

A. Determine the weight of sludge solids/m² of fill as:

$$M_s = (FH)\ (Ds)\ (1 - W_s)$$

where:

M_S = weight of sludge solids (kg/m²)
FH = fill height (m)
D_S = density of sludge (kg/m³)
W_S = water content of sludge (kg/kg)

$$M_s = (3.46\ m)\ (1012\ kg/m^3)\ (1 - 0.95)$$

$$= 175.08\ kg/m^2$$

B. Calculate the mass of each contaminant/m² of fill material as:

$$M = (M_s)\ (N)$$

where:

M = mass of contaminant in fill (g/m²)
N = dry weight contaminant concentration in sludge (mg/kg)

Benzene

$$M = (175.08\ kg/m^2)\ (3.0\ mg/kg)\ (0.001\ g/mg)$$

$$= 0.53\ g/m^2$$

C. Calculate the volume of water/m^2 present in the fill at the time of disposal as:

$$V_{W1} = [(W_s)(M_s)]/[(Dw)(1 - W_s)]$$

where:

V_{W1} = volume of water/m^2 present in the fill (m^3/m^2)

D_w = density of water (kg/m^3)

$V_{W1} = [(0.95)(175.08\ kg/m^2)]/[(1000\ kg/m^3)(1 - 0.95)]$

$= 3.33\ m^3/m^2$

D. Calculate the volume of water/m^2 present in the fill after the sludge drains as:

$$V_{W2} = [(S)(M_s)]/[(D_s)(1 - S)]$$

where:

V_{W2} = volume of water/m^2 in the fill after it drains (m^3/m^2)

S = storage capacity of sludge (kg/kg)

$V_{W2} = [(0.9)(175.08\ kg/m^2)]/[(1000\ kg/m^3)(1 - 0.9)]$

$= 1.58\ m^3/m^2$

E. Calculate the volume of water/m^2 that will drain from the sludge as:

$$Dv = V_{W1} - V_{W2}$$

where:

D_v = volume of water/m^2 that drains from the sludge (m^3/m^2)

$D_v = 3.33\ m^3/m^2 - 1.58\ m^3/m^2$

$= 1.75\ m^3/m^2$

F. Calculate the leachable mass/m^2 for each contaminant as:

$$M_L = M - (X)(D_v)$$

where:

M_L = leachable mass/m² (g/m²)
X = contaminant concentration in leachate (mg/ℓ)

Benzene

$$M_L = 0.53\ g/m^2 - (0.05\ g/m^3)\ (1.75\ m^3/m^2)$$
$$= 0.44\ g/m^2$$

G. Calculate the period of time needed to leach the leachable mass from the landfill. For nondegradable contaminants the formula is:

$$T_p = M_L/(R)\ (X)$$

For degradable contaminants the formula is:

$$T_p = \frac{-1}{\lambda} \ln\ \{[(R)\ (X)]/[(R)\ (X) + (\lambda)\ (M_L)]$$

where:

T_p = leach time (pulse time) (years)
R = net recharge (m/year)
X = leachate concentration (g/m³ = mg/ℓ)
λ = degradation rate constant (year⁻¹)

Benzene

$$T_p = \frac{1}{3.9\ year^{-1}} \ln \frac{(0.5\ m/year)\ (0.05\ g/m^3)}{(0.5\ m/year)\ (0.05\ g/m^3) + (3.9\ year^{-1})\ (0.44\ g/m^2)}$$

$= 1.09$ year

4.5.1.2.2. Unsaturated Zone Calculations --

A. Calculate the steady-state moisture content of the soil for each layer in the unsaturated zone as:

$$f = f_s \left(\frac{R}{K_{sat}}\right)^{[1/(2b + 3)]}$$

where:

F = steady-state moisture content (m³/m³)

f_s = saturated moisture content for the unsaturated zone soil (m^3/m^3)

K_{sat} = saturated hydraulic conductivity of the unsaturated zone soil (m/year)

b = negative 1 times the slope of the log-log plot of matric potential and saturated moisture content (dimensionless)

Layer 1

$$f = 0.39\ m^3/m^3 \ \frac{0.5\ m/year}{10^{[illegible]}\ m/year}^{1/[(2)(4) + 3]}$$

$$= 0.16\ m^3/m^3$$

(If multiple layers are present in the unsaturated zone, solve for each layer.)

B. Calculate the steady-state travel time of the water across each unsaturated zone soil layer as:

$$T_u = (hy)\ (\theta)/R$$

where:

T_u = steady-state travel time across an unsaturated zone soil layer (years)

hy = depth to groundwater or thickness of the unsaturated zone beneath the landfill (m)

Layer 1

$$T_{u1} = (1.0\ m)\ (0.16\ m^3/m^3)/(0.5\ m/year)$$

$$= 0.32\ year$$

(If multiple layers are present in the unsaturated zone, solve for each layer.)

C. Calculate the total travel time of the water across the unsaturated zone as:

$$T_T = T_{u1} + T_{u2} + \ldots$$

where:

T_T = total travel time across all layers of the unsaturated zone (years)

$$T_T = 0.32 \text{ year}$$

D. Calculate the average velocity of the water across the unsaturated zone as:

$$V_{ave} = (hy_1 + hy_2 + \ldots)/T_T$$

where:

V_{ave} = average velocity across the unsaturated zone (m/year)
hy# = thickness of each unsaturated zone layer where # = 1, 2, ...

$$V_{ave} = 1.0 \text{ m}/0.32 \text{ year}$$

$$= 3.14 \text{ m/year}$$

E. Calculate the average moisture content of the unsaturated zone as:

$$f_{ave} = R/V_{ave}$$

where:

f_{ave} = average moisture content of the unsaturated zone (m^3/m^3)

$$f_{ave} = \frac{0.5 \text{ m/year}}{3.14 \text{ m/year}}$$

$$= 0.16 \text{ m}^3/\text{m}^3$$

F. Obtain the unsaturated zone distribution coefficient, Kd, and unsaturated zone degradation rate for each contaminant from the scientific literature. Select Kd values based on soil type. If there is more than one type of soil (i.e., more than one layer) in the unsaturated zone, use a weighted average for Kd. Calculate the weighted average by summing the products of the thickness of each layer and the Kd for each soil type (layer) and dividing by the total thickness of all layers.

Contaminant	Kd (ℓ/kg)	Degradation Rate (year^{-1})
Benzene	$7.4\text{x}10^{-3}$	3.9

G. Calculate the retardation factor for the contaminant in the unsaturated zone as:

$$RF = 1 + (B_u\ Kd/f_{ave})$$

where:

RF = retardation factor (dimensionless)
B_u = bulk density of unsaturated zone material (kg/m^3)
Kd = distribution coefficient (ℓ/kg)

If multiple layers are present in the unsaturated zone, calculate a weighted average retardation factor using weighted average values for bulk density and saturated moisture content (weight according to layer thickness).

Benzene

$$RF = 1 + \frac{7.4\text{x}10^{-3}\ \ell/\text{kg})\ (0.001\ \text{m}^3/\ell)\ (1400\ \text{kg/m}^3)}{0.39\ \text{m}^3/\text{m}^3}$$

$$= 1.03$$

H. For degradable contaminants, calculate the concentration of contaminant leaving the unsaturated zone accounting for degradation as:

$$C_{us} = X \exp\ [(-1)\ (\lambda)\ (T_T)\ (RF)]$$

where:

C_{us} = contaminant concentration exiting the unsaturated zone (mg/ℓ)

Benzene

$$C_{us} = 0.05\ \text{mg}/\ell\ \exp\ [(-1)\ (3.9\ \text{year}^{-1})\ (0.32\ \text{year})\ (1.03)]$$
$$= 0.014\ \text{mg}/\ell$$

4.5.1.2.3. MINTEQ Adjustment for Geochemical Reactions -- For metallic contaminants, determine the amount of concentration reduction that will occur due to geochemical reactions in the saturated flow system (aquifer) using the MINTEQ graphs given in Appendix B (Figures B-2 through B-6).

4.5.1.2.4. **Tier 2 Intermediate Comparison to Reference Water Concentrations** -- Compare the Tier 2 concentrations at the base of the unsaturated zone, as calculated without allowing for dispersion, with the reference water concentration. The final Tier 2 concentrations for benzene are given in H on the preceding page.

Benzene

Concentration after allowing for decay = 0.014 mg/ℓ

Reference Water Concentration = 0.000673 mg/ℓ

For benzene, the Tier 2 concentrations at the base of the unsaturated zone, without accounting for dispersion, are greater than the reference water concentration. Therefore, the Tier 2 analysis needs to be continued using the CHAIN and AT123D models.

4.5.1.2.5. **CHAIN Model** -- Since the Tier 2 result presented above is not below the reference water concentration, it is necessary to run the CHAIN analytical transport model to predict the contamination concentration at the base of the unsaturated zone. The input data required by the CHAIN model are the leachate concentration (X), the net recharge (R) as the flux rate, the leach time out of the landfill (T_p) as the input pulse time, the retardation factor (RF) and the degradation rate (λ). The dispersion coefficient used in CHAIN is calculated as one-tenth the depth to groundwater (unsaturated zone thickness, hy) times the average groundwater velocity in the unsaturated zone (V_{ave}).

For organic contaminants, compare the maximum model-predicted concentration to the reference water concentration values. If the model-predicted concentration is less than the reference water concentration, no further Tier 2 analysis is required. If not, the saturated transport model AT123D should be run.

For inorganic contaminants, take the maximum model predicted concentrations and enter the appropriate curves in Appendix B (Figures B-2 through B-6) to predict the resulting concentration after geochemical reaction. If the resulting concentration is less than the threshold, no further Tier 2 analysis is required. If not, the resulting concentrations should be entered into the saturated transport model AT123D.

The CHAIN model results for this example problem are as follows:

Dependable Organics	Unsaturated Model Results (mg/ℓ)	Reference Water Concentration (mg/ℓ)
Benzene	0.015	0.000673

The unsaturated model results for benzene are above the reference concentration value; therefore, the saturated transport code AT123D needs to be run for benzene.

4.5.1.2.6. AT123D **Model** -- Since the CHAIN model results are not below the reference concentration for benzene, it is necessary to run the AT123D saturated zone transport model to predict the contaminant concentration at the facility boundary. The peak contaminant concentrations and the pulse time as predicted by the CHAIN model are used as inputs to AT123D. The other input data required by AT123D are the degradation rates (λ), the retardation factors (calculated for the saturated zone using the saturated distribution coefficient, bulk density and porosity), the groundwater velocity (calculated as the saturated hydraulic conductivity times the hydraulic gradient divided by the effective porosity), the longitudinal dispersion coefficient (calculated as one-tenth the distance to the landfill boundary times the groundwater velocity), and the transverse and vertical dispersion coefficients (calculated as one-tenth the longitudinal dispersion coefficient).

The AT123D model results for the example problem are as follows:

Degradable Organics	Saturated Model Results (mg/ℓ)	Reference Water Concentration (mg/ℓ)
Benzene	9.8×10^{-8}	0.000673

The saturated model results for benzene are well below the reference water concentration. Therefore, this application would be acceptable. If the predicted output concentrations were very close to the criteria values, the permit writer may require a characterization of input parameter uncertainty and additional runs to determine sensitivity to that uncertainty.

If background concentrations of benzene are present in the groundwater, these concentrations would be added to the saturated model results and this total concentration would be compared to the reference water concentration.

4.5.2. **National Criteria Site-Specific Application.** In order to set national criteria, the methodology is applied in reverse order with the same site- and chemical-specific inputs. In this case the starting point is the environmental concentration (EC) criteria and the endpoint is the acceptable leachate concentration or the acceptable amount of total contaminant in the landfill. Example calculations for the trial scenario follow for benzene. The input data for this application are provided in Table 4-10.

Benzene

The first step of the methodology was to run the CHAIN code to predict the peak benzene concentration and the release duration of benzene into the saturated flow system. Pulse times of 0.01, 0.1, 1 and 10 years and contaminant concentrations of 0.00079 and 0.0079 mg/ℓ were used as input to

TABLE 4-10

CHAIN Model Results for the National Criteria Calculation for Benzene

Pulse Time (years)	Input Concentration (mg/ℓ)	Peak Output Concentration (mg/ℓ)	Release Duration (years)
0.01	0.00079	0.11×10^{-4}	0.7
0.01	0.0079	0.11×10^{-3}	0.7
0.1	0.00079	0.98×10^{-4}	0.8
0.1	0.0079	0.98×10^{-3}	0.8
1.0	0.00079	0.24×10^{-5}	1.6
1.0	0.0079	0.24×10^{-2}	1.6
10.0	0.00079	0.24×10^{-3}	10.0
10.0	0.0079	0.24×10^{-2}	10.0

CHAIN. Pulse times of 0.01 and 0.1 years are not realistic, but they were simulated for illustrative purposes since, as will be discussed, all pulse times >1 year yield the same peak concentration at the facility boundary.

The CHAIN model results are listed in Table 4-11. The peak concentration for pulse times of 1 and 10 years are identical and would be the same for all pulse times >10 years. The reason for this is that the benzene travel time through the unsaturated system is short (0.3 years) compared to pulse times >1 year; therefore, there is little dispersive effect and an equilibrium concentration is reached in the flow system.

The second step is to use the peak concentration and release time from CHAIN as the input concentration and pulse time to AT123D. Since AT123D requires an input flux rate, the actual input to AT123D is the peak output concentration from CHAIN multiplied by the recharge rate (0.5 m/year).

The output from AT123D is a series of peak concentrations (X_f) for each of the cases simulated as shown in Table 4-11. Table 4-11 also lists the pulse times and input concentrations (X_i) used in the CHAIN model.

The third step of the national criteria methodology is to plot the pairs of points (X_i vs. X_f) for identical pulse times in Table 4-11. The data points produce three curves as shown in Figure 4-5; the curves for pulse times of 1 and 10 years overlay each other. The curves for 1 and 10 years also represent all pulse times >10 years.

The maximum benzene concentration for all pulse times >1 year that would not exceed the health effects criteria of 0.000673 mg/ℓ can be determined as follows. Locate the point on the 1-year pulse time curve whose abscissa is equal to the health effects criteria for benzene. The ordinate of this point is the maximum allowable leachate concentration for pulse times ≥ 1

TABLE 4-11

AT123D Model Results for the National Criteria Calculation for Benzene

Pulse Time (years)	CHAIN Model Input Concentration (X_i) (mg/ℓ)	AT123D Model Peak Output Concentration (X_f) (mg/ℓ)
0.01	0.00079	6.7×10^{-12}
0.01	0.0079	6.7×10^{-11}
0.1	0.00079	6.0×10^{-11}
0.1	0.0079	6.0×10^{-10}
1.0	0.00079	1.5×10^{-10}
1.0	0.0079	1.5×10^{-9}
10.0	0.00079	1.5×10^{-10}
10.0	0.0079	1.5×10^{-9}

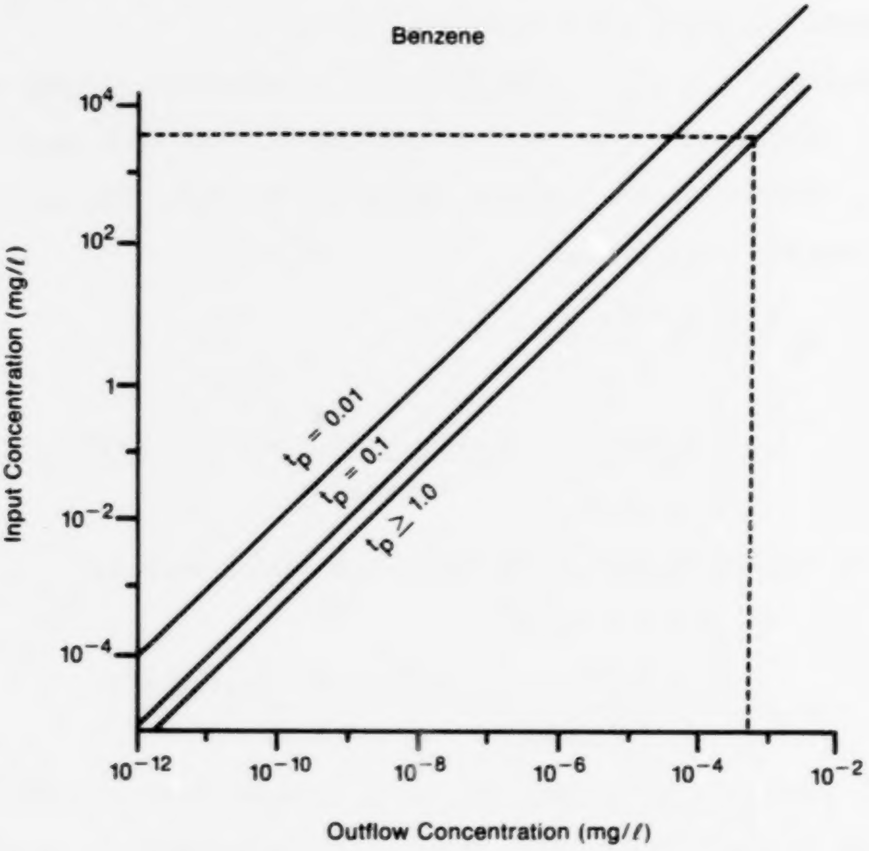


FIGURE 4-5

Graph of the Family of Curves for the Benzene National Criteria Calculations year (see dotted lines in Figure 4-5). The maximum allowable benzene concentration in the landfill is 4000 mg/ℓ. Pulse times of <1 year are probably not realistic and are not considered.

To check this result, the CHAIN and AT123D models were run with a pulse length of 1 year and a benzene input concentration of 4000 mg/ℓ. The peak concentration at the property boundary was calculated to be 0.00075 mg/ℓ, just above the health effects criteria limit.

The final step of the calculation was to determine the total mass (M) of benzene that could be present in the landfill and still meet the health effects criteria at the property boundary. The total leachable mass (M_L) of benzene was calculated as:

$$M_L = \frac{X_i\ R\ (e^{\lambda T_p} - 1)}{\lambda}$$

$$= \frac{(4000\ \text{mg}/\ell)\ (0.5\ \text{m/year})\ [e^{(3.9\ \text{year}^{-1})\ (1\ \text{year})} - 1]}{3.9\ \text{year}^{-1}}$$

$$= 24{,}800\ \text{g/m}^2$$

The total mass of benzene in the landfill was calculated as:

$$M = M_L + X_i\ D_v$$

$$= 24{,}800\ \text{g/m}^2 + (4000\ \text{mg}/\ell)\ (1.75\ \text{m}^3/\text{m}^2)$$

$$= 31{,}800\ \text{g/m}^2$$

The total mass of benzene that can be present in the landfill and still be close to the health effects criteria at the boundary is quite large due to the rapid decay time for benzene, which has a half-life of approximately 65 days.

It should be noted that benzene solubility in water is reported as 820 mg/ℓ. Therefore, if other sludge constituents do not significantly increase benzene's solubility, these criteria will not restrict the landfilling of any benzene-containing sludges for this set of site conditions.

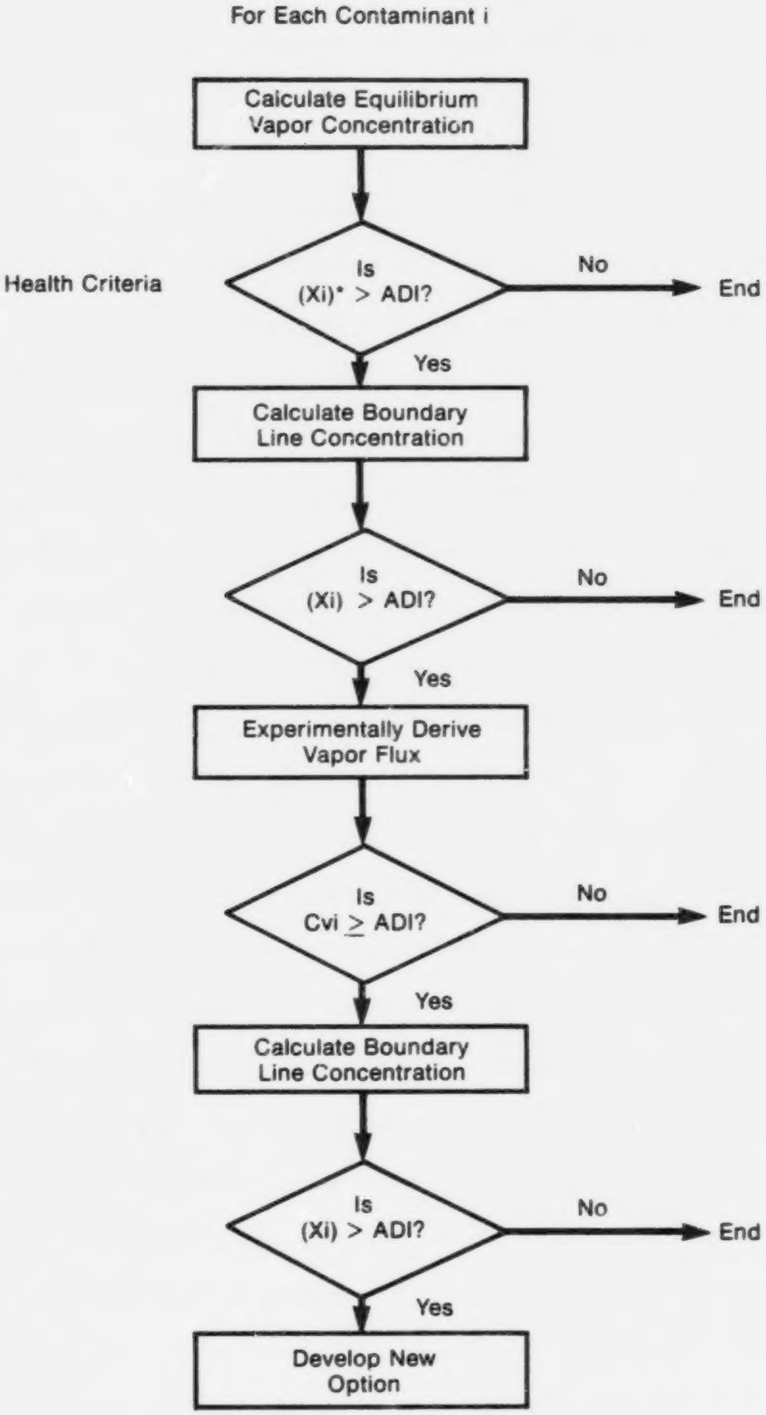
5. METHODOLOGY FOR PREDICTING THE VAPOR CONTAMINANT PATHWAY

5.1. OVERVIEW OF THE METHOD

Vapor loss from the landfill has been identified as a possible pathway of concern for migration of certain volatile toxic chemicals (e.g., benzene, cyanide, dimethylnitrosamine and trichloroethylene) from sludge disposal/reuse. In concert with the risk assessment framework provided here, the tiered approach and concern for chronic exposure, three levels of analysis are outlined. As in the case of groundwater contamination, the initial tier is a simple comparative structure that can be implemented to quickly screen a chemical for the landfilling option. Contaminants failing Tier 1 can be evaluated at Tier 2 to consider site-specific conditions.

Regardless of the level of assessment (Tiers 1 through 3), the basic approach requires some degree of simulation of the movement of vapors up from the waste into the atmosphere and downwind to the property boundary. The property boundary has been selected as the point of compliance, since that would be the first area of unrestricted access where continuous exposure is likely to occur. Workers would be exposed potentially to higher concentrations on the landfill property, but that contact is regulated under OSHA, would be limited to a 40-hour work week, and should be controlled through use of respirators as appropriate. Chronic risk at the property boundary is measured against the selected health effects threshold value. This approach parallels that taken to evaluate landfill bans and exemption requests for hazardous wastes.

The tiered approach and sequencing of the overall methodology is illustrated in Figure 5-1. Tier 1 involves a simple partial pressure calculation using Henry's Law to predict maximum potential vapor levels above the


For Each Contaminant i
Calculate Equilibrium Vapor Concentration
Health Criteria
Is (Xi)* > ADI?
No
End
Yes
Calculate Boundary Line Concentration
Is (Xi) > ADI?
No
End
Yes
Experimentally Derive Vapor Flux
Is Cvi ≥ ADI?
No
End
Yes
Calculate Boundary Line Concentration
Is (Xi) > ADI?
No
End
Yes
Develop New Option

*(Xi) = Concentration of Contaminant i in Atmosphere

FIGURE 5-1

Logic Flow for Vapor Loss Pathway Evaluation of Landfilled Sludges sludge. This is a very conservative estimate of concentration, since it does not account for air/sludge matrix partitioning or dispersion in the atmosphere. If the Tier 1 concentrations are lower than the threshold value, no further evaluation of the contaminant is necessary. If the predicted concentration exceeds the threshold value, the applicant may opt to proceed to Tier 2 where transport through the soil cover and atmospheric dispersion are taken into consideration.

The Tier 2 analysis employs an analytical model developed to evaluate vapor loss and dispersion from hazardous waste sites as a part of the landfill ban analysis (Environmental Science and Engineering, 1985). Elements of the model consider those periods when the cell face is open, the period of temporary cover and the postclosure period. Degradation and deposition are not accounted for since travel times will be relatively short.

The procedures and details of each tier in the methodology are described in the following sections.

5.2. ASSUMPTIONS

In order to apply a methodology such as that presented here, it is necessary to make simplifying assumptions. The assumptions, stated or implied, required to implement the vapor pathway analysis are outlined in Table 5-1 and discussed in the following sections.

5.2.1. Vapor Pressure. The Tier 1 and Tier 2 methodologies require the vapor pressure (vapor concentration) of the contaminant to be specified. Because vapor pressures are not routinely measured, the methodologies use Henry's Law to specify vapor concentration as a function of liquid concentration. Henry's Law is most appropriate for low aqueous concentrations and low solids content sludges. As the concentrations and solids contents increase, Henry's Law will tend to overpredict vapor pressure as a result of

TABLE 5-1

Assumptions for the Vapor Pathway Methodology

Functional Area	Assumptions	Ramifications
Vapor Pressure	Vapor concentration can be defined as a function of liquid concentration by use of Henry's Law.	Is appropriate for low concentrations and low solids contents. As concentrations and solids contents increase, method will tend to overpredict vapor concentrations. Variations will also arise from temperature and pressure changes.
Loss Rate	Tier 2 assumes that loss rate after emplacement of soil cover is controlled by diffusion through soil.	Is appropriate assumption for landfilling.
Atmospheric Transport	Tier 1 assumes no atmospheric dilution.	Will grossly overpredict exposure, as is consistent with Tier 1 approach.
	Tier 2 assumes constant wind speed and direction and that receptor is located downwind along centerline of plume.	Assumption predicts maximum possible exposure to receptor.
	Tier 2 assumes stable atmospheric conditions.	Assumption predicts maximum possible downwind concentrations.

activity effects and partitioning between solid and liquid phases. As such, the use of Henry's Law represents a conservative approach.

5.2.2. Loss Rate. The Tier 2 methodology assumes that the loss rate of contaminants following emplacement of the soil cover is controlled by diffusion of contaminants through the soil. The loss rate is then independent of wind speed. This assumption is not appropriate for describing direct volatilization from solid or liquid surfaces and, therefore, is not used to describe losses during the active period of disposal. The assumption is appropriate for describing volatile losses when contaminants must first diffuse to the atmosphere and is, therefore, appropriate for describing losses from a landfill. It is, however, recognized that some absorption and degradation of organic vapors within the soil cover would occur, thereby decreasing the concentration of air emissions. Unfortunately, little is known of these processes, so the conservative approach is taken here.

The Tier 2 methodology assumes that the final soil cover applied to a landfill cell has the same permeability as the temporary soil cover. In practice, the final soil cover should not be more permeable than the temporary cover and will usually be less permeable. This assumption, therefore, will lead to an overprediction of loss rates.

5.2.3. Atmospheric Transport. The Tier 1 methodology assumes no atmospheric dilution of contaminants. The result of this assumption will be to grossly overpredict atmospheric contaminant concentrations. This approach is clearly conservative and is consistent with the Tier 1 approach.

To simplify use of the atmospheric transport model in Tier 2, it is assumed that the wind speed and direction are constant and that the receptor of concern is always located downwind along the center line of the plume. The effect of these assumptions is to predict the maximum possible downwind atmospheric concentrations and, therefore, the maximum possible exposure. This conservative approach is consistent with the other exposure methodologies.

In applying the atmospheric model, it is assumed that stable atmospheric conditions will always be encountered. The effect of this assumption will be to maximize the resulting downwind concentrations, thereby predicting the maximum possible exposure levels. Again, this conservative approach is consistent with other exposure methodologies.

5.3. CALCULATIONS

5.3.1. Tier 1. The first tier embodies a simple comparison of source term vapor concentrations to the threshold value. Source term vapor concentrations are predicted on the basis of sludge contaminant concentrations and Henry's Law. This does not account for any dispersion in the atmosphere and, thereby, overpredicts concentrations. Henry's Law describes vapor compositions over dilute solutions. The relation is given as:

$$P_i = H_i Cl_i \tag{5-1}$$

where:

P_i = partial pressure of i above the solution (atm)
H_i = Henry's Law Constant for i (atm-m³/mol)
Cl_i = concentration of i in the solution (mol/m³)

Assuming the vapor phases act as ideal gases, the partial pressure can be translated into an atmospheric concentration using Dalton's Law:

$$P_i = y_i P \tag{5-2}$$

where:

y_i = mole fraction of i in the gas phase (dimensionless)
P = total pressure in the system (atm)

For the landfill environment of interest here, P can be set at 1 atm. Then combining Equations 5-1 and 5-2, atmospheric concentration (y_i) can be calculated as:

$$Py_i = H_i Cl_i \tag{5-3}$$

With the molecular weight of the contaminant and air and the molar volume of air, this can be converted to an atmospheric concentration in terms of weight fraction or mass per volume.

An alternate approach is to use a dimensionless modified Henry's Law Constant (H') defined as:

$$H' = Cv_i/Cl_i \tag{5-4}$$

where:

Cv_i = concentration of i in air (mass/volume)
Cl_i = concentration of i in water (mass/volume)

This eliminates the need for conversions to obtain the atmospheric concentration of the contaminant in the desired units. H can be converted to H' by using the Universal Gas Law to calculate atmospheric concentration (mol/volume) from partial pressure.

The use of the Henry's Law approach assumes ideal gas behavior and dilute solutions. Both assumptions are appropriate for the levels of volatile contaminants expected in municipal sludge, since handling and treatment prior to disposal are likely to have allowed high concentrations to diminish through the vaporization process. In empirical work with municipal sludge, English et al. (1980) found Henry's Law to be useful in predicting atmospheric concentrations of ammonia. Values for the Henry's Law Constant can be obtained from the literature or calculated from physical properties. Henry's Law Constants and modified Henry's Law Constants for contaminants of interest are provided in Appendix B.

The Henry's Law approach is likely to overpredict vapor concentrations because the organic solids in sludge will bind some of the contaminants, making them less available in the water solution for volatilization. Because the prediction is conservative, it provides a greater margin of safety. Underprediction would occur if the contaminant were present in the liquid phase only and the solids comprised a major fraction of the overall solution. This is not the case for the sludges anticipated. The estimated vapor concentrations are compared to the appropriate reference air concentration (RAC). If the vapor concentrations do not exceed the RAC, no further analysis is required. If the vapor concentrations do exceed the RAC, the applicant can decide if the greater accuracy of Tier 2 or 3 is likely to be advantageous and, therefore, worth the added cost.

5.3.2. Tier 2. The first-tier methodology treats the landfilled sludge as though it were a solution in a surface impoundment. The vapor concentrations of contaminant are a result of direct volatilization from the surface and subsequent diffusion into the air column. In reality, the sludge will reside in a landfill cell. The active face of the cell may remain uncovered for short periods of time (<8 hours), but will soon receive a layer of soil overburden that will remain intact throughout the postclosure period. In some cases, a tighter capping material will be added and vegetation established as a part of the final cover. In either event, a finite layer of soil will reside between the sludge's surface and the air column. All vapors lost from the sludge must migrate through the cover to reach the atmosphere and be available for downwind transport.

In considering vapor loss from hazardous waste landfills, Environmental Science and Engineering (1985) depicted three discrete phases for which predictive constructs were devised: operating period with uncovered wastes, operating period with shallow temporary cover, and postclosure period with permanent cover. Since regulations do not require impermeable caps for sludge or municipal refuse landfills, the permanent cover may not differ significantly from the temporary cover with respect to vapor losses. The permanent cover will likely include revegetation and a greater total thickness. The analytical methodology used to predict vapor migration through the temporary cover is the same as that used for the permanent cover. Therefore, two analytical procedures are presented for the Tier 2 evaluation, one for predicting vapor loss from an open landfill cell and one for predicting vapor migration through a soil cover.

Two types of exposure are evaluated during the Tier 2 analysis. The first evaluation addresses the exposure due to losses during the active operating period for a landfill cell. This exposure will be characterized by relatively high loss rates (primarily from the uncovered waste) and relatively small surface areas (i.e., the area of the active cell). The second evaluation will be of the exposure due to losses from the covered wastes during the postclosure period. This exposure is characterized by relatively low loss rates from the covered wastes and relatively large surface areas (i.e., the surface area of the entire closed landfill).

According to Environmental Science and Engineering (1985), the loss rate from uncovered wastes during the active life of the landfill can be calculated as:

$$q_{a_i} = \frac{0.17\ v\ (0.994)^{T-20}\ Cv_i}{\sqrt{MW_i}} \qquad (5\text{-}5)$$

where:

q_{a_i} = emission rate during active uncovered period for contaminant i (g/m^2-sec)

ν = windspeed (m/sec)

T = temperature (°C)

T-20 = a temperature correction factor derived empirically

Cv_i = vapor concentration of contaminant i (g/m³)

MW_i = molecular weight of contaminant i

From Equation 5-3, Cv_i can be determined from the liquid concentration of contaminant i, Cl_i and Henry's Law Constant for contaminant i, H_i. Equation 5-5 can then be expressed as:

$$qai = \frac{0.17\ \nu\ (0.994)^{T-20}\ H_i Cl_i}{\sqrt{MW_i}} \tag{5-6}$$

The emission rate for vapors emanating through cover materials during the active and postclosure period can be calculated as (Environmental Science and Engineering, 1985):

$$qpi = \frac{9.2 \times 10^{-5}\ n_a^{10/3}\ Cv_i (1.006)^{T-20}}{tc\ n^2 \sqrt{MW_i}} \tag{5-7}$$

where:

q_{pi} = emission rate through landfill cover to contaminant i (g/m²-sec)

n_a = air filled porosity of cover soil (cm³/cm³)

Cv_i = vapor concentration

T = temperature (°C)

T-20 = a temperature correction factor derived empirically

tc = thickness of cover (m)

n = total porosity of cover soil (cm³/cm³)

MW_i = molecular weight of contaminant i

As with Equation 5-6, the vapor concentration can be expressed in terms of the liquid concentration and Henry's Law Constant to yield:

$$qpi = \frac{9.2 \times 10^{-5} \, n_a^{10/3} \, (1.006)^{T-20} \, H_i Cl_i}{tc \, n^2 \, \sqrt{MW_i}} \qquad (5\text{-}8)$$

The contaminant emission rate for the active and postclosure periods calculated using either Equation 5-6 or 5-8 is used to calculate atmospheric concentrations at the compliance point using a source-receptor ratio (SRR).*

$$C(X)i = q \times SRR \qquad (5\text{-}9)$$

where C(X)i is the atmospheric concentration ($\mu g/m^3$), X is the downstream distance from the source to the receptor (m) and SRR is calculated as (Environmental Science and Engineering, 1985):

$$SRR = 2.032 \times 10^6 \left[\frac{X_0^2 V}{(r' + Xy) \, \nu \, \sigma z}\right] \qquad (5\text{-}10)$$

where:

X_0 = the characteristic length of the landfill assumed to be a square (m)

V = vertical term which is a function of source height and z

r' = distance from the landfill center to the receptor or point of compliance (m)

X_y = lateral virtual distance (m)

ν = mean wind speed (m/s)

σ_z = standard deviation of the vertical concentration distance (m)

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*If the landfill is vent, the total emission $Q_{pci} = q_{pci}(1-fv) + q_{vent}$. q_{vent} is derived as $q_{vent} = [0.082U/ MW \, H'C_{1i} \, (0.994)^{T-20}$, and fv is the fraction of the fill that is vented.

As with Equation 5-6, the vapor concentration can be expressed in terms of the liquid concentration and Henry's Law Constant to yield:

$$qpi = \frac{9.2 \times 10^{-5}\ n_a^{10/3}\ (1.006)^{T-20}\ H_i Cl_i}{tc\ n^2\ \sqrt{MW_i}} \qquad (5\text{-}8)$$

The contaminant emission rate for the active and postclosure periods calculated using either Equation 5-6 or 5-8 is used to calculate atmospheric concentrations at the compliance point using a source-receptor ratio (SRR).*

$$C(X)i = q \times SRR \qquad (5\text{-}9)$$

where C(X)i is the atmospheric concentration ($\mu g/m^3$), X is the downstream distance from the source to the receptor (m) and SRR is calculated as (Environmental Science and Engineering, 1985):

$$SRR = 2.032 \times 10^6 \left[\frac{X_o^2 V}{(r' + Xy)\ \nu\ \sigma z}\right] \qquad (5\text{-}10)$$

where:

X_o = the characteristic length of the landfill assumed to be a square (m)

V = vertical term which is a function of source height and z

r' = distance from the landfill center to the receptor or point of compliance (m)

X_y = lateral virtual distance (m)

ν = mean wind speed (m/s)

σ_z = standard deviation of the vertical concentration distance (m)

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*If the landfill is vent, the total emission $Q_{pci} = q_{pci}(1\text{-}fv) + q_{vent}$. q_{vent} is derived as q_{vent} = [0.082U/ MW $H'C_{1i}$ $(0.994)^{T-20}$, and fv is the fraction of the fill that is vented.

The vertical term for gases, V, is set at

$$V = \frac{(\sqrt{2\pi})\ (\sigma_Z)}{2L} \quad \text{for } \sigma_Z/L \geq 1.6 \tag{5-11}$$

and

$$V = e^{\left[-1/2\left(\frac{H}{\sigma_Z}\right)^2\right]} + \sum_{n=1}^{\infty} \left\{ 2e^{[-1/2(\frac{2nL}{\sigma_Z})^2]} \right\} \tag{5-12}$$

where L = mixing layer height (m).

The lateral virtual distance, Xy, is calculated as:

$$X_y = \left(\frac{X_o}{\pi}\right) \text{Cot} \left(\frac{\Delta Ø'}{2}\right) \tag{5-13}$$

where ΔØ' = sector width (radians) for 22.5° Ø' = 0.393.

The standard deviation in the vertical distance, σ_z, can be taken from tables for various distances and stability classes or calculated as indicated in Table 5-2.

5.3.3. **Procedure.** In order to establish sludge concentration criteria for volatile contaminants, it is once again necessary to operate the methodology provided here in a reverse mode just as described for the groundwater pathway in Chapter 4. That is, the RAC must be taken as input to determine the maximum allowable concentration in the source sludge. From Equation 5-9, the compliance point concentration is defined as:

$$C = Q \times SRR \tag{5-14}$$

Since SRR is characteristic of a site and not concentration dependent, a single value can be calculated for a representative site. When C is set at C_{ET}, the effects threshold concentration, the allowable flux, Q, is defined as:

$$Q = C_{ET}/SRR \tag{5-15}$$

TABLE 5-2

Parameters Used to Calculate σ_Z [a]

Pasquill Stability Category	x (km)	$\sigma_Z = a\ x\ (mb)^b$	
		a	b
Very unstable[b]	0.10 - 0.15	158.080	1.04520
	0.16 - 0.20	170.222	1.09320
	0.21 - 0.25	179.520	1.12620
	0.26 - 0.30	217.410	1.26440
	0.31 - 0.40	258.890	1.40940
	0.41 - 0.50	346.750	1.72830
	0.51 - 3.11	453.850	2.11660
	3.11	+	+
Unstable[b]	0.10 - 0.20	90.673	0.93198
	0.21 - 0.40	98.483	0.98332
	0.40	109.300	1.09710
Slightly unstable[b]	0.10	62.141	0.91465
Neutral	0.10 - 0.30	34.459	0.86974
	0.31 - 1.00	32.093	0.81066
	1.01 - 3.00	32.093	0.64403
	3.01 - 10.00	33.504	0.60586
	10.01 - 30.00	36.650	0.56589
	30.00	44.053	0.51179
Slightly stable	0.10 - 0.30	23.331	0.81956
	0.31 - 1.00	21.628	0.75660
	1.01 - 2.00	21.628	0.63077
	2.01 - 4.00	22.534	0.57154
	4.01 - 10.00	24.703	0.50527
	10.01 - 20.00	26.970	0.46713
	20.01 - 40.00	35.420	0.37615
	40.00	47.618	0.29592

TABLE 5-2 (cont.)

Pasquill Stability Category	x (km)	$\sigma_z = a\ x\ (mb)^b$	
		a	b
Stable	0.10 - 0.20	15.209	0.81558
	0.21 - 0.70	14.457	0.78407
	0.71 - 1.00	13.953	0.68465
	1.01 - 2.00	13.953	0.63227
	2.01 - 3.00	14.823	0.54503
	3.01 - 7.00	16.187	0.46490
	7.01 - 15.00	17.836	0.41507
	15.01 - 30.00	22.651	0.32681
	30.01 - 60.00	27.084	0.27436
	60.00	34.219	0.21716

[a] Source: Environmental Science and Engineering, 1985

[b] If the calculated value of σ_z exceeds 5000 m, σ_z is set to 5000 m.

+ = σ_z is equal to 5000 m.

It has been found that the flux during the active life of the facility is greater than that during postclosure, and will, therefore, be the limiting factor. From Equation 5-6:

$$q_{ai} = \frac{0.17\ \nu\ (0.994)^{T-20}\ H_i Cl_i}{\sqrt{MW_i}} \qquad (5\text{-}16)$$

where:

q_{ai} = allowable flux during the active period for contaminant i (g/m²-sec)
ν = windspeed (m/sec)
T = temperature (°C)
H_i = Henry's Law Constant (dimensionless)
Cl_i = concentration of contaminant in the sludge liquid (mg/ℓ)
MW_i = molecular weight of contaminant

Combining Equations 5-6 and 5-15 for the criteria case yields:

$$C_{ET}/SRR = \frac{0.17\ \nu\ (0.994)^{T-20}\ H_i Cl_i}{\sqrt{MW_i}} \qquad (5\text{-}17)$$

which can be solved for Cl_i to give Cl_{iET}, the limiting sludge liquid concentration:

$$Cl_{iET} = \frac{C_{ET}\ (\sqrt{MW_i})}{SRR\ (0.17\ \nu)(0.994)^{T-20}\ H_i} \qquad (5\text{-}18)$$

5.4. INPUT PARAMETER REQUIREMENTS

5.4.1. Fate and Transport: Pathway Data.

1. Vertical Term for Transport (V) -- It is conservatively assumed that atmospheric conditions are stable. Therefore, V will always be equal to 1.

2. Lateral Virtual Distance (X_y) -- Equal to X_o [Cot $(\Delta\theta'/2)]/\sqrt{\pi}$, where $\Delta\theta'$ is the sector width in radians. It is assumed that the sector width is 0.393 (22.5°); therefore, $X_y = 2.84X_o$.

3. Average Wind Speed (ν) -- Obtained from local weather station.

4. Average Air Temperature (T) -- Obtained from local weather station.

5. Air-Filled Porosity of Cover Soil (n_a) -- It is assumed that cover soils will be drained to field capacity. Therefore, the air-filled porosity is assumed to be equal to the effective porosity (n_e). Values for effective porosity can be obtained from Table 4-5.

6. Porosity of Cover Soil (n) -- Can be measured in the laboratory or obtained from Table 4-5.

7. Cover Thickness (tc) -- Obtained from site design or operating procedures.

8. Length or Width of Source (X_0) -- Obtained from site map or plans. It is assumed that source areas are square. For active, uncovered case, X_0 is equal to the square root of the area of an individual landfill cell. For postclosure, covered case, X_0 is equal to the square root of the area of the overall landfill.

9. Distance from Center of Source to Receptor (r') -- Obtained from site plans. r' is taken as the sum of one-half the width of the total landfill area ($X_0/2$) plus the width of the buffer area from the landfill area to the property boundary.

10. Standard Deviation of the Vertical Concentration Distance (σ_z) -- Atmospheric conditions are assumed to be stable.

5.4.2. Fate and Transport: Chemical-Specific Data.

1. Contaminant Concentration in Sludge Liquid (C_l) -- Derived directly for a contaminant by applying the TCLP. Alternately, C_l can be calculated from the dry weight contaminant concentration, C_s, the organic carbon distribution coefficient for the contaminant, K_{oc}, the fraction of organic carbon in the sludge solids, f_{oc}, and the solids content of the sludge, S.

2. Henry's Law Constant (H') -- Obtained from Appendix B or derived directly.

3. Molecular Weight of Contaminant (MW) -- Obtained from the literature.

5.4.3. **Health Effects Data.** A reference air concentration (RAC, in mg/m^3), will be defined as an ambient air concentration used to evaluate the potential for adverse effects on human health as a result of sludge landfilling. That is, for a given landfill site, and given the practice definitions and assumptions stated previously in this methodology, the criterion for a given sludge contaminant is that concentration in the sludge that cannot be exceeded, and is calculated to result in air concentrations below the RAC at a compliance point downwind from the site. Exceeding the RAC would be a basis for concern that adverse health effects may occur in a human population in the site vicinity.

RAC is determined, based upon contaminant toxicity and air inhalation rate, from the following general equation:

$$\text{Reference Air Concentration: } RAC = I_p/I_a \qquad (5\text{-}19)$$

where I_p is the acceptable chronic pollutant intake rate (in mg/day) based on the potential for health effects and I_a is the air inhalation rate (in m^3/day). This simplified equation assumes that the inhaled contaminant is absorbed into the body via the lungs at the same rate in humans as in the experimental species tested, or between routes of exposure (e.g., oral and inhalation). Also, this equation assumes that there are no other exposures of the contaminant from other sources, natural or manmade. I_p varies according to the pollutant evaluated and according to whether the pollutant acts according to a threshold or nonthreshold mechanism of toxicity.

5.4.3.1. THRESHOLD-ACTING TOXICANTS -- Threshold effects are those for which a safe (i.e., subthreshold) level of toxicant exposure can be estimated. For these toxicants, RAC is derived as follows:

$$\text{Reference Air Concentration: } RAC = \left[\left(\frac{RfD \times bw}{RE}\right) - TBI\right] \div I_a \qquad (5\text{-}20)$$

where:

RfD = reference dose (mg/kg/day)

bw = human body weight (kg)

TBI = total background intake rate of pollutant from all other sources of exposure (mg/day)

I_a = air inhalation rate (m^3/day)

RE = Relative effectiveness of inhalation exposure (unitless)

The definition and derivation of each of the parameters used to estimate RAC for threshold-acting toxicants are further discussed below.

5.4.3.1.1. Reference Dose (RfD) -- When toxicant exposure is by ingestion, the threshold assumption has traditionally been used to establish an acceptable daily intake, or ADI. The Food and Agricultural Organization and the World Health Organization have defined ADI as "the daily intake of a chemical which, during an entire lifetime, appears to be without appreciable risk on the basis of all the known facts at the time. It is expressed in milligrams of the chemical per kilogram of body weight (mg/kg)" (Lu, 1983). Procedures for estimating the ADI from various types of toxicological data were outlined by the U.S. EPA in 1980 (U.S. EPA, 1980c). More recently the Agency has preferred the use of a new term, the "reference dose," or RfD, to avoid the connotation of acceptability, which is often controversial.

The RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of the daily exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious effects during a lifetime. The RfD is expressed in units of mg/kg bw/day. The RfD is estimated from observations in humans whenever possible. When human data are lacking, observations in animals are used, employing uncertainty factors as specified by existing Agency methodology.

RfD values for noncarcinogenic (or systemic) toxicity have been derived by several groups within the Agency. An Intra-Agency Work Group verifies each RfD, which is then loaded onto the Agency's publically available

Integrated Risk Information System (IRIS) database. Most of the noncarcinogenic chemicals that are presently candidates for sludge criteria for the landfill pathway are included on the Agency's RfD list, and thus no new effort will be required to establish RfDs for deriving sludge criteria. For any chemicals not so listed, RfD values should be derived according to established Agency procedures (U.S. EPA, 1988).

5.4.3.1.2. **Human Body Weight (bw) and Air Inhalation Rate (I_a)** -- An assumption of 20 m^3 inhalation/day by a 70-kg adult has been widely used in Agency risk assessments and will be used in this methodology for adults. Table 5-3 shows values of I_a for a typical man, woman, child and infant with a typical activity schedule, as defined by the International Commission on Radiological Protection (ICRP, 1975). Additional values have been derived for an adult with the same activity schedule, but using upper limit rather than average assumptions about respiration rates for each activity, and for an adult with normal respiration rates, but whose work is moderately active and who practices 1 hour of heavy activity (i.e., strenuous exercise) per day (Fruhman, 1964, as cited Diem and Lentner, 1970; Åstrand and Rodahl, 1977, as cited in Fiserova-Bergerova, 1983). Representative body weights have been assigned to each of these individuals to calculate a respiratory volume-to-body weight ratio. (These ratios have been derived for illustrative purposes only.) The resulting ratio values range from 0.33 to 0.47 m^3/kg/day, all of which exceed the ratio value of 0.29 m^3/kg/day estimated from the 70-kg adult inhaling 20 m^3/day, as used currently by the Agency. Therefore, the typically assumed values for adults may underestimate actual exposure. In cases where children or infants are known to be at specific risk, it may be more appropriate to use values of bw and I_a for children or infants.

TABLE 5-3

Daily Respiratory Volumes for "Reference" Individuals (Normal Individuals at Typical Activity Levels) and for Adults with Higher-than-Normal Respiratory Volume or Higher-than-Normal Activity Levels (Volumes in m³)

	"Reference" Man[a]	"Reference" Woman[a]	Upper-Limit Adult	Active Adult	"Reference" Child[a] (10 years)	"Reference" Infant[a] (1 year)
8-hour working, light activity	9.6	9.1	12.0[b]	--	6.24	2.5 (10 hours)
8-hour working, moderate activity	--	--	--	14.4[c]	--	--
8-hour nonoccupational (light) activity	9.6	9.1	12.0[b]	--	6.24	--
7-hour nonoccupational (light) activity	--	--	--	8.4	--	--
1-hour heavy activity	--	--	--	2.5[c]	--	--
8-hour rest	3.6	2.9	7.0[d]	3.6	2.3	1.3 (14 hours)
Total daily respiratory volume	22.8	21.1	31.0	28.9	14.78	3.8
Body weight (kg)	70	58	65	65	33	10
Ratio of Volume to body weight[e]	0.33	0.36	0.47	0.44	0.45	0.38

[a] Source: ICRP, 1975

[b] Upper-limit values for "ordinary man or woman," for "light" activity category (Åstrand and Rodahl, 1977, as cited in Fiserova-Bergerova, 1983)

[c] Averaged values for "ordinary man or woman," for "moderate" or "heavy" activity categories (Åstrand and Rodahl, 1977)

[d] Upper 95th percentile for adults, age 20-39 years, at rest (Fruhman, 1964, as cited in Diem and Lentner, 1970)

[e] The inhalation volume to body weight ratios have been derived from the referenced values for illustrative purposes only.

5.4.3.1.3. Total Background Intake Rate of Pollutant (TBI) -- It is important to recognize that sources of exposure other than sludge disposal practices may exist, and that the total exposure should be maintained below the RfD. Other sources of exposure include background levels (whether natural or anthropogenic) in drinking water, food or air. Other types of exposure, due to occupation or habits such as smoking, might also be included depending on data availability and regulatory policy. These exposures are summed to estimate TBI.

Data for estimating background exposure usually are derived from analytical surveys of surface, ground or tap water, from FDA market-basket surveys and from air-monitoring surveys. These surveys may report means, medians, percentiles or ranges, as well as detection limits. Estimates of TBI may be based on values representing central tendency or on upper-bound exposure situations, depending on regulatory policy. Data chosen to estimate TBI should be consistent with the value of bw. Where background data are reported in terms of a concentration in air or water, ingestion or inhalation rates applicable to adults or children can be used to estimate the proper daily background intake value. Where data are reported as total daily dietary intake for adults and similar values for children are unavailable, conversion to an intake for children may be required. Such a conversion could be estimated on the basis of relative total food intake or relative total caloric intake between adults and children.

For example, in deriving the National Emission Standard for mercury, the average dietary contribution of 10 μg Hg/70 kg/day was subtracted from the assumed threshold of 30 μg/70 kg/day to give an allowable increment from inhalation exposure of 20 μg/70 kg/day. An assumed inhalation volume of

20 m^3/day for a 70-kg man was then applied to derive an allowable ambient air concentration of 1 µg Hg/m^3 (U.S. EPA, 1984a). For the purposes of this methodology, however, TBI should be an estimate of background exposure from all sources, including inhalation.

As stated in the beginning of this subsection, the TBI is the summed estimate of all possible background exposures, except exposures resulting from a sludge disposal practice. To be more exact, the TBI should be a summed total of all toxicologically effective intakes from all nonsludge exposures. To determine the effective TBI, background intake values (BI) for each exposure route must be divided by that route's particular relative effectiveness (RE) factor. Thus, the TBI can be mathematically derived, after all the background exposures have been determined, using the following equation:

$$TBI = \frac{BI\ (food)}{RE\ (food)} + \frac{BI\ (water)}{RE\ (water)} + \frac{BI\ (air)}{RE\ (air)} + \ldots + \frac{BI\ (n)}{RE\ (n)} \qquad (5\text{-}21)$$

where:

TBI = total background intake rate of pollutant from all other sources of exposure (mg/day)

BI = background intake of pollutant from a given exposure route, indicated by subscript (mg/day)

RE = relative effectiveness, with respect to inhalation exposure, of the exposure route indicated by subscript (unitless)

5.4.3.1.4. Fraction of Inhaled Air from Contaminated Area -- It is recognized that an individual exposed to air emissions from a landfill may not necessarily remain in the landfill proximity for 24 hours/day. However, if it is assumed that residential areas may be contaminated, it is likely that less mobile individuals will include those at greatest risk. Therefore, it is reasonable to assume that 100% of the air breathed by the MEIs will be from the area of the landfill.

5.4.3.1.5. Relative Effectiveness of Exposure (RE) -- RE is a unitless factor that shows the relative toxicological effectiveness of an exposure by a given route when compared to another route. The value of RE may reflect observed or estimated differences in absorption between the inhalation and ingestion routes, which can then significantly influence the quantity of a chemical that reaches a particular target tissue, the length of time it takes to get there, and the degree and duration of the effect. The RE factor may also reflect differences in the occurrence of the critical toxicological effects at the portal of entry. For example, carbon tetrachloride and chloroform were estimated to be 40% and 65% as effective, respectively, by inhalation as by ingestion based on high-dose absorption differences (U.S. EPA, 1984b,c). In addition to route differences, RE can also reflect differences in the exposure matrix. For example, absorption of nickel ingested in water has been estimated to be 5 times that of nickel ingested in the diet (U.S. EPA, 1985d). The presence of food in the gastrointestinal tract may delay absorption and reduce the availability of orally administered compounds, as demonstrated for halocarbons (NRC, 1986).

Physiologically based pharmacokinetic (PB-PK) models have evolved into particularly useful tools for predicting disposition differences due to exposure route differences. Their use is predicated on the premise that an effective (target-tissue) dose achieved by one route in a particular species is expected to be equally effective when achieved by another exposure route or in some other species. For example, the proper measure of target-tissue dose for a chemical with pharmacologic activity would be the tissue concentration divided by some measure of the receptor binding constant for that chemical. Such models account for fundamental physiologic and biochemical parameters such as blood flows, ventilatory parameters, metabolic capacities and renal clearance, tailored by the physicochemical and biochemical properties of the agent in question. The behavior of a substance administered by a different exposure route can be determined by adding equations that describe the nature of the new input function. Similarly, since known physiologic parameters are used, different species (e.g., humans vs. test species) can be modeled by replacing the appropriate constants. It should be emphasized that PB-PK models must be used in conjunction with toxicity and mechanistic studies in order to relate the effective dose associated with a certain level of risk for the test species and conditions to other scenarios. A detailed approach for the application of PB-PK models for derivation of the RE factor is beyond the scope of this document, but the reader is referred to the comprehensive discussion in NRC (1986). Other useful discussions on considerations necessary when extrapolating route to route are found in Pepelko and Withey (1985) and Clewell and Andersen (1985).

Since exposure for the vapor pathway is by inhalation, the RE factors applied are all with respect to the inhalation route. Therefore, the value of RE in Equation 5-20 gives the relative effectiveness of the exposure route and matrix on which the RfD was based when compared to inhalation of contaminated air. Similarly, the RE factors in Equation 5-21 show the relative effectiveness, with respect to the inhalation route, of each background exposure route and matrix.

An RE factor should only be applied where well-documented, referenced information is available on the contaminant's observed relative effectiveness or its pharmacokinetics. When such information is not available, RE is equal to 1.

5.4.3.2. CARCINOGENS -- For carcinogenic chemicals, the Agency considers the excess risk of cancer to be linearly related to dose, except at high-dose levels (U.S. EPA, 1986a). The threshold assumption, therefore, does not hold, as risk diminishes with dose but does not become zero or background until dose becomes zero.

The decision whether to treat a chemical as a threshold- or nonthreshold-acting (i.e., carcinogenic) agent depends on the weight of the evidence that it may be carcinogenic to humans. Methods for classifying chemicals as to their weight of evidence have been described by U.S. EPA (U.S. EPA, 1986a), and most of the chemicals that presently are candidates for sludge criteria have recently been classified in Health Assessment Documents or other reports prepared by the U.S. EPA's Office of Health and Environmental Assessment (OHEA), or in connection with the development of recommended maximum contaminant levels (RMCLs) for drinking-water contaminants (U.S. EPA, 1985e). To derive values of the reference air concentration (RAC), a decision must be made as to which classifications constitute sufficient evidence for basing a quantitative risk assessment on a presumption of carcinogenicity. Chemicals in classifications A and B, "human carcinogen" and "probable human carcinogen," respectively, have usually been assessed as carcinogens, whereas those in classifications D and E, "not classifiable as to human carcinogenicity because of inadequate human and animal data" and "evidence of noncarcinogenicity for humans," respectively, have usually been assessed according to threshold effects. Chemicals classified as C, "possible human carcinogen," have received varying treatment. For example, lindane, classified by the Human Health Assessment Group (HHAG) of the U.S. EPA as B2-C, or between the lower range of the B category and category C, has been assessed using both the linear model for tumorigenic effects (U.S. EPA, 1980b) and based on threshold effects (U.S. EPA, 1985e). Table 5-4 gives an illustration of these U.S. EPA classifications based on the available weight of evidence.

Using the weight-of-evidence classification without noting the explanatory material for a specific chemical may lead to a flawed conclusion, since some of the classifications are exposure-route dependent. Certain compounds (e.g., nickel) have been shown to be carcinogenic by the inhalation route, but not by ingestion. The issue of whether or not to treat an agent as carcinogenic by ingestion remains controversial for several chemicals.

If a pollutant is to be assessed according to nonthreshold, carcinogenic effects, the RAC is derived as follows:

$$\text{Reference Air Concentration: } RAC = \left[\left(\frac{RL \times bw}{q_1{}^* \times RE}\right) - TBI\right] \div I_a \qquad (5\text{-}22)$$

where:

$q_1{}^*$ = human cancer potency $[(mg/kg/day)^{-1}]$

RL = risk level (unitless) (e.g., 10^{-5}, 10^{-6}, etc.)

bw = human body weight (kg)

RE = relative effectiveness of inhalation exposure (unitless)

I_a = air inhalation rate (m^3/day)

TBI = total background intake rate of pollutant (mg/day), from all other sources of exposure

The RAC, in the case of carcinogens, is thought to be protective since the $q_1{}^*$ is typically an upper-limit value (i.e., the true potency is considered unlikely to be greater and may be less). The definition and derivation

TABLE 5-4

Illustrative Categorization of Evidence Based on Animal and Human Data*

Human Evidence	Animal Evidence				
	Sufficient	Limited	Inadequate	No Data	No Evidence
Sufficient	A	A	A	A	A
Limited	B1	B1	B1	B1	B1
Inadequate	B2	C	D	D	D
No data	B2	C	D	D	E
No evidence	B2	C	D	D	E

*The above assignments are presented for illustrative purposes. There may be nuances in the classification of both animal and human data indicating that different categorizations than those given in the table should be assigned. Furthermore, these assignments are tentative and may be modified by ancillary evidence. In this regard, all relevant information should be evaluated to determine if the designation of the overall weight of evidence needs to be modified. Relevant factors to be included along with the tumor data from human and animal studies include structure-activity relationships; short-term test findings; results of appropriate physiological, biochemical and toxicological observations; and comparative metabolism and pharmacokinetic studies. The nature of these findings may cause an adjustment of the overall categorization of the weight of evidence.

of each of the parameters used to estimate RAC for carcinogens are further discussed in the following subsections.

5.4.3.2.1. **Human Cancer Potency** (q_1*) -- For most carcinogenic chemicals, the linearized multistage model is recommended for estimating human cancer potency from animal data (U.S. EPA, 1986a). When epidemiological data are available, potency is estimated based on the observed relative risk in exposed vs. nonexposed individuals, and on the magnitude of exposure. Guidelines for use of these procedures have been presented in the U.S. EPA (1980c, 1985e) and in each of a series of Health Assessment Documents prepared by OHEA (e.g., U.S. EPA, 1985d). The true potency value is considered unlikely to be above the upper-bound estimate of the slope of the dose-response curve in the low-dose range, and it is expressed in terms of risk/dose, where dose is in units of mg/kg/day. Thus, q_1* has units of $(mg/kg/day)^{-1}$. OHEA has derived potency estimates for each of the potentially carcinogenic chemicals that are presently candidates for sludge criteria. Therefore, no new effort will be required to develop potency estimates to derive sludge criteria.

5.4.3.2.2. Risk Level (RL) -- Since by definition no "safe" level exists for exposure to nonthreshold agents, values of RAC are calculated to reflect various levels of cancer risk. If RL is set at zero, then RAC will be zero. If RL is set at 10^{-6}, RAC will be the concentration which, for lifetime exposure, is calculated to have an upper-bound cancer risk of one case in one million individuals exposed. This risk level refers to excess cancer risk, i.e., over and above the background cancer risk in unexposed individuals. By varying RL, RAC may be calculated for any level of risk in the low-dose region, i.e., RL $\leq 10^{-2}$. Specification of a given risk level on which to base regulations is a matter of policy. Therefore, it is common practice to derive criteria representing several levels of risk without specifying any level as "acceptable."

5.4.3.2.3. Human Body Weight (bw) and Air Inhalation Rate (I_a) -- Considerations for defining bw and I_a are similar to those stated in Section 5.4.3.1.2. The HHAG assumes respective values of 70 kg and 20 m^3/day to derive unit risk estimates for air, which are potency estimates transformed to units of $(\mu g/m^3)^{-1}$. As illustrated in Table 5-3, exposures may be higher in children than in adults when the ratios of inhalation volumes to body weights are compared. However, because exposure is lifelong, values of bw and I_a are usually chosen to be representative of adults.

5.4.3.2.4. Relative Effectiveness of Exposure (RE) -- RE is a unitless factor that shows the relative toxicological effectiveness of an exposure by a given route when compared to another route. The value of RE may reflect observed or estimated differences in absorption between the inhalation and ingestion routes, which can significantly influence the quantity of a chemical that reaches a particular target tissue, the length of time it takes to get there, and the degree and duration of the effect. The RE factor may also reflect differences in the occurrence of critical toxicological effects at the portal of entry. For example, carbon tetrachloride and chloroform were estimated to be 40% and 65% as effective, respectively, by inhalation as by ingestion based on high-dose absorption differences (U.S. EPA, 1984b,c). In addition to route differences, RE can also reflect differences in the exposure matrix. For example, absorption of nickel ingested in water has been estimated to be 5 times that of nickel ingested in food (U.S. EPA, 1985d). The presence of food in the gastrointestinal tract may delay absorption and reduce the availability of orally administered compounds, as demonstrated for halocarbons (NRC, 1986).

PB-PK models have evolved into particularly useful tools for predicting disposition differences due to exposure route differences. Their use is predicated on the premise that an effective (target-tissue) dose achieved by one route in a particular species is expected to be equally effective when achieved by another exposure route or in some other species. For example, the proper measure of target-tissue dose for a chemical with pharmacologic activity would be the tissue concentration divided by some measure of the receptor binding constant for that chemical. Such models account for fundamental physiologic and biochemical parameters such as blood flows, ventilatory parameters, metabolic capacities and renal clearance, tailored by the physicochemical and biochemical properties of the agent in question. The behavior of a substance administered by a different exposure route can be determined by adding equations that describe the nature of the new input function. Similarly, since known physiologic parameters are used, different species (e.g., humans vs. test species) can be modeled by replacing the appropriate constants. It should be emphasized that PB-PK models must be used in conjunction with toxicity and mechanistic studies in order to relate the effective dose associated with a certain level of risk for the test species and conditions to other scenarios. A detailed approach for the application of PB-PK models for derivation of the RE factor is beyond the scope of this document, but the reader is referred to the comprehensive discussion in NRC (1986). Other useful discussions on considerations necessary when extrapolating route to route are found in Pepelko and Withey (1985) and Clewell and Andersen (1985).

Since exposure for the vapor pathway is by inhalation, the RE factors applied are all with respect to the inhalation route. Therefore, the value of RE in Equation 5-22 gives the relative effectiveness of the exposure route and matrix on which the q_1* was based when compared to inhalation of contaminated air. Similarly, the RE factors in Equation 5-21 show the relative effectiveness, with respect to the inhalation route, of each background exposure route and matrix.

An RE factor should only be applied where well-documented, referenced information is available on the contaminant's observed relative effectiveness or its pharmacokinetics. When such information is not available, RE is equal to 1.

5.4.3.2.5. Total Background Intake Rate of Pollutant (TBI) -- It is important to recognize that sources of exposure other than sludge disposal practices may exist, and that the total exposure should be maintained below the determined cancer risk-specific exposure level. Other sources of exposure include background levels (whether natural or anthropogenic) in drinking water, food or air. Other types of exposure, due to occupation or habits such as smoking, might also be included depending on data availability and regulatory policy. These exposures are summed to estimate TBI.

Data for estimating background exposure usually are derived from analytical surveys of surface, ground or tap water, from FDA market-basket surveys, and from air-monitoring surveys. These surveys may report means, medians, percentiles or ranges, as well as detection limits. Estimates of TBI may be based on values representing central tendency or on upper-bound exposure situations, depending on regulatory policy. Data chosen to estimate TBI should be consistent with the value of bw. Where background data are reported in terms of a concentration in air or water, ingestion or inhalation rates applicable to adults can be used to estimate the proper daily background intake value. For certain compounds (e.g., nickel) that have been shown to be carcinogenic by the inhalation route, but not by the ingestion route, the TBI should not include background exposure from the ingestion route. Thus, in such a case only background exposures from other air emission sources should be included in the TBI.

As stated in the beginning of this subsection, the TBI is the summed estimate of all possible background exposures, except exposures resulting from a sludge disposal practice. To be more exact, the TBI should be a summed total of all toxicologically effective intakes from all nonsludge exposures. To determine the effective TBI, background intake values (BI) for each exposure route must be divided by that route's particular relative effectiveness (RE) factor. Thus, the TBI can be mathematically derived, after all the background exposures have been determined, using the following equation:

$$\mathrm{TBI} = \frac{\mathrm{BI\ (food)}}{\mathrm{RE\ (food)}} + \frac{\mathrm{BI\ (water)}}{\mathrm{RE\ (water)}} + \frac{\mathrm{BI\ (air)}}{\mathrm{RE\ (air)}} + \ldots + \frac{\mathrm{BI\ (n)}}{\mathrm{RE\ (n)}} \qquad (5\text{-}23)$$

where:

TBI = total background intake rate of pollutant from all other sources of exposure (mg/day)

BI = background intake of pollutant from a given exposure route, indicated by subscript (mg/day)

RE = relative effectiveness, with respect to inhalation exposure, of the exposure route indicated by subscript (unitless)

5.4.3.2.6. Fraction of Inhaled Air From Contaminated Area -- It is recognized that an individual exposed to air emissions from a landfill may not necessarily remain in the landfill proximity for 24 hours/day. However, if it is assumed that residential areas may be contaminated, it is likely that less mobile individuals will include those at greatest risk. Therefore, it is reasonable to assume that 100% of the air breathed by the MEIs will be from the area of landfill.

5.5. SITE-SPECIFIC APPLICATION

This section presents sample calculations for determining the vapor exposure resulting from landfilling of sludge. In the following, calculations are first made for a particular landfill on a site-specific application and then an example is given for calculating maximum allowable contaminant levels in sludge. Benzene, because it is a volatile contaminant of concern, is used for the example calculations. For the examples, data describing the occurrence and concentration of benzene in sludge are taken from U.S. EPA (1985a). The pathway and chemical parameters used in the calculations are summarized in Table 5-5. Data describing waste sites are values assumed to represent reasonable cases. In actual practice, the data used in the calculations would be those measured or collected by the applicant.

Assume operating procedures include excavation of a 4- by 16-m trench, disposal of three daily 0.5-m lifts in each trench, application of a daily cover of 0.3 m soil and application of a final cover of 1.0 m soil. Assume that 67% of the total disposal site area is available for trenches (Table 5-6).

5.5.1. Tier 1 Calculation. The Tier 1 calculation involves comparing the equilibrium vapor concentration of the constituent with the reference air concentration (RAC). This approach represents the worst possible case with no allowance made for atmospheric dilution, dispersion or degradation. The

TABLE 5-5

Input Parameters for Example Calculations: Vapor Loss

Fate and Transport: Pathway Data		
1.	Vertical term for transport	$V = 1$
2.	Lateral virtual distance	$X_y = 2.84x_o$ $x_o = 22.64$ m active 1361.46 m postclosure
3.	Average windspeed	$\nu = 2$ m/sec
4.	Average air temperature	$T = 15°C$
5.	Air-filled porosity of cover soil	$n_a = 0.1$
6.	Porosity of cover soil	$n = 0.4$
7.	Cover thickness	$T_c = 0.3$ m active, 1.0 m postclosure
8.	Length of source	$X_o = 8$ m active, 480 m postclosure
9.	Distance from center of source to receptor	$r' = 340$ m
10.	Standard deviation of the vertical concentration distance	$\sigma_z = 6.2$ m
Fate and Transport: Chemical-Specific Data (Benzene)		
11.	Contaminant concentration in sludge liquid	$X = 0.0083$ mg/ℓ
12.	Henry's Law Constant	$H' = 0.24$
13.	Molecular weight of contaminant	$MW = 78$
Health Data (Benzene)		
14.	Reference concentration in air	$RAC = 6.73x10^{-2}$ μg/m^3

TABLE 5-6

Supporting Sludge Landfill Characteristics

Daily disposal rate	10 dry metric tons/day
Trench dimensions	4 m by 16 m
Depth of daily fill	0.5 m
Life of facility	20 years
Total trench area	156,000 m^2
Total disposal site area	234,000 m^2

equilibrium vapor concentration is taken as the product of the Henry's Law Constant of the constituent and the liquid phase concentration of the constituent.

The liquid phase constituent concentration can be obtained in several ways. If the leachate extraction procedure is used, the liquid concentration will be determined directly from the procedure. If the analytical results are expressed in terms of dry weight, it will be necessary to convert the dry weight results to an equivalent liquid phase concentration accounting for partitioning between the liquid and solid phases. This is accomplished with Equation 5-24:

$$C_l = \frac{C_{dry}\, S}{K_{oc}\, f_{oc}\, S + \frac{(1-S)}{\gamma_\ell}} \qquad (5\text{-}24)$$

where:

C_l = concentration of contaminant in sludge liquid (mg/ℓ)

C_{dry} = dry weight concentration of contaminant in sludge (mg/kg)

S = solids content of sludge (kg dry solids/kg total wet sludge)

K_{oc} = organic carbon distribution coefficient

$$\frac{\text{mg contaminant/kg organic carbon}}{\text{mg contaminant/}\ell\text{ sludge liquid}}$$

f_{oc} = organic carbon content of sludge (kg organic carbon/kg sludge solids)

γ_ℓ = density of sludge liquid (kg sludge liquid/ℓ sludge liquid)

For the example calculation, the mean dry weight concentration of benzene in sludge, 0.326 mg/kg, reported in U.S. EPA (1985a) is used. The organic carbon distribution coefficient for benzene is 74.2 ℓ/kg (U.S. EPA, 1985a). Assuming a solids content of 30% for dewatered sludge, an organic carbon content of 50% for the sludge solids and a density of 1 kg/ℓ for the sludge liquid, the equivalent liquid concentration is the following:

$$C_l = \frac{(0.326\ \text{mg/kg})(0.30\ \text{kg/kg})}{(74.2\ \ell/\text{kg})(0.5\ \text{kg/kg})(0.30\ \text{kg/kg}) + \frac{(1-0.30)\ \text{kg/kg}}{1.0\ \text{kg}/\ell}}$$

$$= 0.0083\ \text{mg}/\ell$$

The Henry's Law Constant for benzene is then used to calculate the vapor concentration in equilibrium with the liquid concentration:

$$C_v = H\ C_l \qquad (5\text{-}25)$$

From Appendix B, the dimensionless Henry's Law Constant for benzene is 0.24. The equilibrium vapor pressure is:

$$C_v = (0.24)\ (0.0083\ \text{mg}/\ell) = 0.0020\ \text{mg}/\ell = 2.0\ \text{mg/m}^3$$

The RAC for the carcinogen benzene is derived using Equation 5-22:

$$\text{RAC} = \left[\left(\frac{\text{RL} \times \text{bw}}{q_1{}^* \times \text{RE}}\right) - \text{TBI}\right] \div I_a$$

The risk level (RL), the body weight (bw) and the daily inhalation volume (I_a) are set for this example at 10^{-6}, 70 kg and 20 m^3, respectively. The relative effectiveness factor (RE) is set at 1. The human cancer potency for benzene has been determined by the U.S. EPA to be 5.2×10^{-2} $(\text{mg/kg/day})^{-1}$. Current total background intake (TBI) of benzene from all other sources (i.e., except from landfilling of sludges) has not been determined for 1986, but for illustrative purposes a TBI of zero is used here to derive an example RAC. Determination of an RAC for a specific landfill site should be based on a current local assessment of TBI.

$$\begin{aligned}\text{RAC} &= \left[\left(\frac{10^{-6} \times 70\ \text{kg}}{5.2\times10^{-2}\ (\text{mg/kg/day})^{-1} \times 1}\right) - 0\right] \div 20\ \text{m}^3 \\ &= 6.73 \times 10^{-5}\ \text{mg/m}^3 \\ &= 6.73 \times 10^{-2}\ \mu\text{g/m}^3 \\ &= 0.0673\ \mu\text{g/m}^3\end{aligned}$$

The above vapor concentration is then compared to the reference value for benzene, RAC = 6.73×10^{-2} $\mu g/m^3$. Since 2 mg/m^3 >> 6.73×10^{-2} $\mu g/m^3$, it is necessary to proceed to Tier 2.

5.5.2. **Tier 2 Calculation.** The Tier 2 methodology involves estimating the flux of contaminant out of the landfill and using an atmospheric dispersion model to predict the atmospheric concentration of contaminant downwind of the site. The long-term average downwind concentration is then compared with the RAC.

The first step of the Tier 2 methodology is to calculate the flux rate of contaminants during the active life of the trench (i.e., before emplacement of final cover). The flux rate for the active period of the cell is taken as the time-weighted average of the flux rate with no cover and the flux rate with temporary daily cover. Under the assumed operating conditions, each trench will be active for a 3-day period. On each of the 3 days, a lift of sludge will be applied followed by a temporary soil cover. It is assumed that the sludge will be uncovered for 4 hours each day. Therefore, the fraction of time that the sludge is uncovered is (3x4)/(3x24) = 0.17. The fraction of time that the sludge is covered by temporary cover is (3x20)/(3x24) = 0.83.

The flux rate during the portion of time that wastes are uncovered is calculated using Equation 5-6:

$$q_{ai} = [0.17\ v\ (0.994)^{T-20}\ H_i C_{1i}]/\sqrt{MWI}$$

Based on the parameter values provided in Tables 5-4 and 5-5, the resulting contaminant flux rate is:

$$\begin{aligned} q_{ai} &= [(0.17)(2\ m/sec)(0.994)^{15-20}(0.24)(0.0083\ g/m^3)]/\sqrt{MWI} \\ &= 7.9 \times 10^{-5}\ g/m^2\text{-sec} \end{aligned}$$

The flux rate during the portion of time that wastes are covered by temporary cover is calculated using Equation 5-8:

$$q_{pi} = [9.2 \times 10^{-5}\ n_a 10/3\ (1.006)^{T-20}\ HC_{1i}]/\sqrt{MWI}\ \ T_c\ n^2$$

As shown in Table 5-5, the thickness of the temporary soil cover, T_c, is 0.3 m. The air-filled porosity of the soil cover, n_a, and the total porosity of the soil cover, n, are assumed to be 0.1 and 0.4, respectively. The resulting contaminant flux rate is:

$$q_{pi} = [(9.2 \times 10^{-5})(0.1)^{10/3}\ (1.006)^{15-20}\ (0.24)(0.0083)]/\left[\sqrt{MWI}\ (0.3)(0.4)^2\right]$$

$$q_{pi} = 2.0 \times 10^{-10}\ g/m^2\text{-sec}$$

The time-weighted flux for the active period is then:

$$(7.9 \times 10^{-5}\ g/m^2\text{-sec})(0.17) + (2.0 \times 10^{-10}\ g/m^2\text{-sec})(0.83)$$

$$= 1.3 \times 10^{-5}\ g/m^2\text{-sec}$$

The second step of the Tier 2 methodology is to calculate the flux rate of contaminants during the postclosure period. The flux during the postclosure period is calculated using Equation 5-8:

$$q_{pi} = [9.2 \times 10^{-5}\ n_a{}^{10/3}\ (1.006)^{T-20}\ H_iC_{1i}]/\left[\sqrt{MWI}\ \ T_c\ n^2\right]$$

The values of variables used will be the same as those used to calculate flux through the temporary cover, except for the cover thickness, T_c. For postclosure, the cover thickness is 1.0 m. The resulting postclosure flux is:

$$q_{pi} = [9.2 \times 10^{-5}\ (0.1)^{10/3}\ (1.006)^{15-20}\ (0.24)(0.0083)]/\left[\sqrt{78}\ (1)(0.4)^2\right]$$

$$= 5.8 \times 10^{-11}\ g/m^2\text{-sec}$$

The long-term average exposure level is based on exposure to contaminants over a 70-year period. The fluxes for the active and postclosure cases, therefore, must be adjusted to reflect the period of exposure. For the active case, one landfill cell will be open at any time during the entire 20-year active period. The long-term average flux associated with the active portion of the fill is then 20/70 times the active flux or:

$$(20/70)(1.3 \times 10^{-5}\ g/m^2\text{-sec}) = 3.71 \times 10^{-6}\ g/m^2\text{-sec}$$

The long-term average flux associated with postclosure will be based on the average postclosure life of the landfill cells. That is, all cells will be closed at least 50 years and the maximum postclosure period will be 70 years. Because the postclosure period varies linearly from 50 to 70 years, the average period of 60 years was used. The long-term average flux associated with postclosure will then be 60/70 of the postclosure flux or:

$$(60/70)(5.8 \times 10^{-11}\ g/m^2\text{-sec}) = 5.0 \times 10^{-11}\ g/m^2\text{-sec}$$

Because the active and postclosure fluxes involve different source areas, the fluxes could not be summed to obtain a single long-term average flux to calculate exposure. That is, the active flux is associated with the area of one landfill cell, while the postclosure flux is associated with the area of the total disposal site. Therefore, the downwind concentrations associated with each flux were calculated and summed to obtain the average exposure.

Downwind exposure concentrations were calculated using Equation 5-9:

$$C_{(r,0)} = (2.032 \times 10^{6}) \left[\frac{X_0^{\,2} q\ V}{(r' + Xy)\ \nu\ \sigma z}\right]$$

The above equation is for the concentration along the center line of the plume, which represents a worst case.

For the active-period exposure, the side of the source area, X_o, is 108 m. In determining the distance from the source center to the receptor, r', it was assumed that the active cell was always located in the center of the disposal area. The distance was then taken as one-half the square root of the area of the disposal site plus a buffer zone distance, assumed to be 100 m.

$$r' = (0.5)\ (234{,}000\ m^2) + 100\ m = 340\ m$$

The lateral virtual distance, X_y, was calculated using Equation 5-13:

$$X_y = \left(\frac{X_0}{\sqrt{\pi}}\right) \text{Cot}\left(\frac{\Delta \emptyset'}{2}\right)$$

$$= 8(2.84) = 22.69 \text{ m}$$

σ_z was calculated for a worst-case condition corresponding to stable atmospheric conditions. For a downwind distance corresponding to the distance r' (0.34 km), σ_z was calculated using the data presented in Table 5-1.

$$\sigma_z = 14.456\ (0.34)^{0.78407} = 6.2 \text{ m}$$

For stable atmospheric conditions and a contaminant release height of 0 m, L is infinite and therefore the vertical term, V, is equal to 1 (Equation 5-11). For the assumed wind speed of 2 m/sec, the resulting downwind concentration is:

$$C_{(r,0)} = (2.032 \times 10^{6})\ \left[\frac{X_0^{2} q\ V}{(r' + X_y)\ \nu\ \sigma_z}\right]$$

$$= \frac{(2.032 \times 10^{6})(8)^{2}\ (3.71 \times 10^{-6})(1)}{(340 + 22.69)(2)(6.2)}$$

$$= 0.11\ \mu\text{g/m}^{3}$$

For the postclosure period, the side of the source area, X_0, is 480 m. The distance from the source center to the receptor, r', is the same as for the active case. As for the active case, the lateral virtual distance, X_y, was calculated using Equation 5-13:

$$X_y = \left(\frac{X_0}{\sqrt{\pi}}\right) \text{Cot}\left(\frac{\Delta \emptyset'}{2}\right) \quad = 480(2.84) = 1361.46 \text{ m}$$

As with the active case, σ_z was selected for a worst-case condition corresponding to stable atmospheric conditions. Because the downwind distance is the same as for the active case, σ_z will be 6.2 m. The vertical term, V, will also be equal to 1, as in the active case. Using the above data and the assumed wind velocity of 2 m/sec, the downwind contaminant concentration is:

$$C_{(r,0)} = 2.032 \times 10^{6} \left[\frac{X_0{}^{2} q \; V}{(r' + X_y) \; \upsilon \; \sigma_Z}\right]$$

$$= \frac{2.032 \times 10^{6} \; (480)^{2} \; (5.0 \times 10^{-11})(1)}{(340 + 1361.46)(2)(6.2)}$$

$$= 1.1 \times 10^{-3} \; \mu g/m^{3}$$

The above results show that the exposure due to the postclosure release is negligible compared to the exposure due to active release. The total exposure concentration for comparison to the reference level will then be the active exposure, or 0.11 $\mu g/m^3$. This is compared to the reference air concentration, RAC = 6.73×10^{-2} $\mu g/m^3$, for benzene.

5.6. NATIONAL CRITERIA SITE-SPECIFIC APPLICATION

To establish sludge concentration criteria for volatile contaminants, it is necessary to operate the methodology provided here in a reverse mode. That is, the RAC must be taken as input to determine the maximum allowable concentration in the source sludge. From Equation 5-14, the compliance point concentration is defined as:

$$C = Q \times SRR$$

Since SRR is characteristic of a site and not concentration dependent, a single value can be calculated for a representative site. When C is set at C_{ET}, the long-term effects threshold concentration, the allowable long-term average flux Q_{ave} is defined as:

$$Q = C_{ET}/SRR \qquad (5\text{-}26)$$

The flux during the active life of the facility was shown in Section 5.5.2. to be far greater than that during postclosure, and therefore the latter may be set equal to zero in the calculation of criteria. From Equation 5-6:

$$q_{ai} = \frac{0.17\ \nu\ (0.994)^{T-20}\ H_i Cl_i}{\sqrt{MW_i}}$$

where:

q_{ai} = flux during the uncovered period (g/m²-sec)
ν = windspeed (m/sec)
T = temperature (°C)
H_i = Henry's Law Constant (dimensionless)
Cl_i = concentration of contaminant in the sludge liquid (mg/ℓ)
MW_i = molecular weight of contaminant

The average flux during the human lifetime is determined by adjusting the uncovered period flux, q_{ai}, for the fraction of time that the sludge is uncovered (0.17) during the facility active life, and for the assumed total active life of the facility (20 years) during the human lifetime (70 years), as described in Section 5.5.2. The resulting relationship is as follows:

$$Q = q_{ai} \times 0.17 \times (20/70) \qquad (5\text{-}27)$$

Combining Equations 5-6, 5-26 and 5-27 for the criteria case yields:

$$C_{ET}/SRR = \frac{0.17\ \nu\ (0.994)^{T-20}\ H_i Cl_i}{\sqrt{MW_i}} \times 0.17 \times \frac{20}{70} \qquad (5\text{-}28)$$

The latter can be solved for Cl_i to give Cl_{iET}, the limiting sludge liquid concentration:

$$Cl_{iET} = \frac{C_{ET}\ (\sqrt{MW_i})}{SRR\ (0.17\ \nu)(0.994)^{T-20} H_i} \times \frac{1}{0.17} \times \frac{70}{20} \qquad (5\text{-}29)$$

For benzene, the MW_i is 78 g/mol, the H_i is 0.24 and the RAC is 6.73×10^{-2} µg/m³. Therefore:

$$Cl_{iET} = \frac{6.73 \times 10^{-2}\ (\sqrt{78})}{(3 \times 10^4)(0.17)(2)(0.994)^{15-20}\ (0.24)} \times \frac{1}{0.17} \times \frac{70}{20} \qquad (5\text{-}30)$$

$$= 4.9 \times 10^{-3}\ \text{mg/ℓ}$$

The national criteria would, therefore, be set at 4.9×10^{-3} mg/ℓ in leachate. Based on Equation 5-24 and assuming a solids content of 30% for dewatered sludge, an organic content of 50% for the sludge solids and a density of 1.0 kg/ℓ for the sludge liquid, the corresponding dry weight concentration of benzene in the landfilled sludge would be 0.19 mg/kg.

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APPENDIX A

COLUMN METHOD FOR DETERMINING RETARDATION FACTOR (RF) AND DISTRIBUTION COEFFICIENT (Kd)

A.1. SCOPE AND APPLICATION

The column methods described herein can be used to experimentally determine the velocity of a contaminant through a column of porous soil/rock. The method is directed to measurement of a retardation factor (the ratio of water velocity to contaminant velocity). A distribution coefficient can subsequently be derived based on the porosity and density of the soil/rock matrix. The method is applicable to any porous media through which water-borne contaminants may flow. Water is passed through a column of the porous media on a once-through or recirculating basis. Contaminant is introduced continuously or as a spike. The time of travel for the contaminant is determined by measuring contaminant in effluent volumes. The result is compared to the velocity of water through the column. The ratio of the two values is defined as the retardation factor.

A.2. THEORY

The column method, which measures the migration velocity of a contaminant (V_c) relative to the groundwater velocity (V_{gw}), provides a retardation factor (RF) according to the following equation:

$$RF = V_{gw}/V_c \tag{A-1}$$

However, when a measurement is made to determine the value of a particular contaminant retardation factor in a rock/groundwater system, the solution's chemical composition (including pH, Eh, cations and anions), the rock's characteristics (chemical composition, mineralogy, surface area, cation and anion exchange capacities) and the equilibrium between rock and groundwater should also be considered. These parameters are important because they can greatly affect the measured value of RF.

Two common expressions used to describe equilibrium adsorption reactions are:

$$S = \frac{abC}{1 + aC} \tag{A-2}$$

and

$$S = KC^{1/n} \tag{A-3}$$

where

S = contaminant concentration sorbed on the rock (μg/g)

C = contaminant concentration in solution (μg/mℓ)

and a, b, K and n are constants.

These equations (Equation A-2 after Langmuir; Equation A-3 after Freundlich) may describe the relationship between S and C for a given solid and solution composition at a constant temperature (often called adsorption isotherms). Both equations are commonly used for an empirical description of experimental adsorption data.

When contaminant concentrations are small, such that aC is <1 in Equation A-2, the isotherm equation reduces to:

$$S = abC \tag{A-4}$$

The exponential constant 1/n in Equation A-3 is usually close to unity, and that equation, too, can be approximated by:

$$S = KC \tag{A-5}$$

Both Equations, A-2 and A-3, can then be approximated by:

$$S = KdC \tag{A-6}$$

where the constants ab and K can be taken as the Kd. It is important to remember that Equation A-6 is usually an approximation and that it holds only under the conditions mentioned above.

When a linear isotherm, such as that given by $S = KdC$, can be used to describe the adsorption reaction, the transport equation for a contaminant in equilibrium with both rock and water in a one-dimensional porous medium flow path is:

$$\left(1 + \frac{bKd}{\theta}\right) \frac{\partial c}{\partial t} = D \frac{\partial^2 C}{\partial x2} + V_{gw} \frac{\partial C}{\partial x} \qquad \text{(A-7)}$$

where

D = dispersion coefficient (cm^2/sec)

x = the distance along the flow path

V_{gw} = groundwater velocity (average pore-water velocity, cm/sec)

b = bulk density (g/cm^3)

θ = porosity of the porous medium

The expression that relates the Kd to the retardation factor,

$$RF = [1 + (b/\theta)\ Kd] \qquad \text{(A-8)}$$

can be substituted into Equation A-7 to obtain a simpler form for the transport equation:

$$RF \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x2} + V_{gw} \frac{\partial C}{\partial x} \qquad \text{(A-9)}$$

If a spike of contaminant is added to the groundwater as it enters the column, adsorption delays the elution of the peak until RF pore volumes have been eluted. The pore volume or void volume of a column is given by the porosity of the porous media (θ) times the total column volume (CV). The retardation factor can then be calculated from the ratio of the volume required to elute the contaminant's peak (or maximum concentration) to the pore volume of that column.

If the porosity is unknown, it can be calculated from:

$$\theta = 1 - b/\rho \qquad \text{(A-10)}$$

where ρ is the average density of the individual particles used to pack the column. An experimental check on the calculated pore volume can be obtained by the elution of a nonsorbing element, which will have a maximum concentration at exactly one pore volume.

In summary, the transport equation for contaminant migration used in most safety assessment models utilizes a linear adsorption isotherm (Equation A-6). Adsorption of the contaminant results in a lower migration velocity for the contaminant than that of the groundwater: $Vr = V_{gw}/RF$. Generally, this is true only when the groundwater composition, rock chemical composition and temperature do not vary (i.e., they are at equilibrium).

A.3. INTERFERENCES

Interferences of two types may occur in the column method: (1) interference in the analysis of eluent for the contaminant of interest, and (2) interaction of the contaminant with the apparatus or column material. In the former case, interferences are identified in the methods prescribed for conducting the analysis required to monitor water for the contaminant. In the latter case, tubing, pumps and column materials must be selected that are compatible with the contaminant of interest. If compatibility cannot be determined from analytical laboratory or materials handling handbooks, a simple laboratory test should be conducted as a blank run. Results of the blank run will indicate if the apparatus itself is retarding or removing contaminant.

A.4. APPARATUS AND MATERIALS

Equipment requirements vary with the selection of high- or low-pressure systems in a single-pass or recirculating mode.

A.4.1. CONTACT COLUMN

A contact column is required to hold the soil/rock matrix during the contact period. A typical low-pressure configuration is depicted in Figure A-1. The column must be constructed of material that will withstand the intended operating pressures and not interact with the groundwater, the contaminant or the soil/rock matrix. For low-pressure experiments, a clear, inert plastic is desirable because it permits direct observation of the column, which will help identify problems with changes in the porous media or bubble entrapment. The upflow configuration is preferred to facilitate bubble migration out of the column. A double layer of screen (inert material such as plastic) should be placed at the ends of the column to disperse flow and reduce the end-cap volume while holding the matrix in place.

The column diameter should be at least 30 times the average particle size of the porous media. The column length should be at least 4 times the column diameter. The column volume should also be selected such that uncertainty about the volume of end-caps and tubing does not greatly affect the estimate of pore volume.

A.4.2. SYSTEM LAYOUT -- LOW-PRESSURE METHODS

Low-pressure column studies require the use of a fluid reservoir, a fluid delivery system, a column and an effluent collection system. Contact with groundwater may be accomplished in a single pass or through use of a recirculating system.

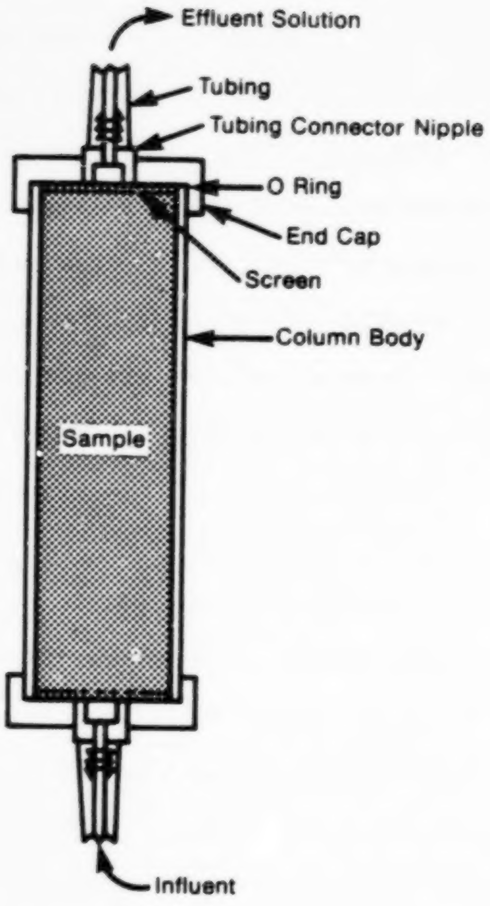
Effluent Solution
Tubing
Tubing Connector Nipple
O Ring
End Cap
Screen
Column Body
Sample
Influent

FIGURE A-1

A Detailed View of the Column Used for Low-Pressure Column Retardation Studies (Single-Pass or Recirculating)

A.4.2.1. Single-Pass Column Method. A schematic of the apparatus needed for a single-pass, low-pressure column method is illustrated in Figure A-2. The reservoir can be constructed of any suitable, nonreacting material for maintaining influent solution. If volatile contaminants are to be studied, an open reservoir will not be suitable unless contaminants are injected in line as a spike. If steady feed methods are employed, a diaphragm system may be required to prevent volatile losses to the atmosphere.

The groundwater velocity through the column is controlled by the hydraulic head gradient [pressure difference between the column's inlet and outlet (ΔH) divided by the column length (L)] and the hydraulic conductivity of the porous media (K) according to:

$$V_{gw} = K \frac{\Delta H}{L} \tag{A-11}$$

A pump is not required for nonvolatile systems if the reservoir is elevated above the column outlet. Such a gravity feed system is practical for heads of up to 50 cm of water. At greater heads, the physical dimensions of the apparatus become limiting, and a pump is more desirable.

The hydraulic conductivity of the soil/rock matrix may also constrain the size/configuration of the apparatus. If small columns (~5 cm) are employed at a head of H = 50 cm water, the practical upper limit to the hydraulic head gradient for a gravity feed system is +H/L = 10 cm water/cm of column. The minimum velocity (Equation 4-10) should be 3×10^{-4} cm/sec, which limits the system to samples having values of $K \geq 3 \times 10^{-5}$ cm/sec. Less permeable media ($K \leq 10^{-5}$ cm/sec) will require a pump. Low-pressure syringe and peristaltic pumps are available that will maintain flow rates over a range suitable for controlling velocities in experiments on relatively permeable columns.

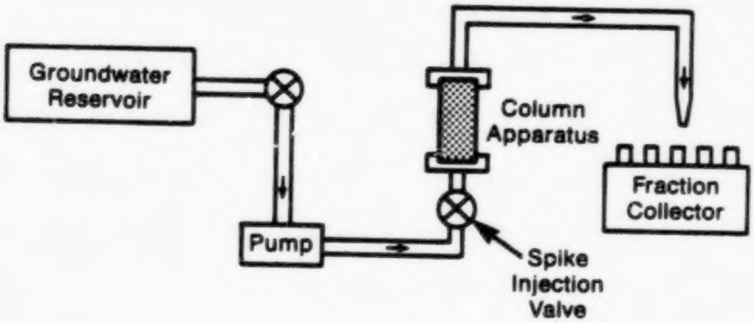
Groundwater Reservoir
Column Apparatus
Fraction Collector
Pump
Spike Injection Valve

FIGURE A-2

Apparatus Needed for a Low-Pressure, Single-Pass Column Retardation Study

The effluent fraction collector can be obtained commercially or may consist of a test-tube rack with tubes that are changed manually. If an automated collector is employed, it should be adjusted to receive small-volume increments (i.e., $v \leq 1/20$ of the calculated pore volume). In this way, the peak centroid (or $C = 1/2\ C_0$ for constant feed) can be narrowed to one or two samples, thus giving no more than 10% uncertainty. Evaporation of sample may be a problem. If holding times are long, a controlled humidity enclosure is required for the collection system. For volatile contaminants, direct injection to an analyzer or accommodations for vapor-tight collection are required.

A.4.2.2. Recirculating Column Method. The recirculating column design is illustrated in Figure A-3. It follows the design of a single-pass column but uses a closed loop from which samples are taken periodically. Flow-rate effects on porosity adsorption kinetics and dispersion may be neglected because very long contact times are possible.

Because the contaminant is in constant contact with tubing, reservoir walls and internal pump parts, special care is required in material selection to minimize interactions. Any adsorption on apparatus will lead to overprediction of retardation and hence the distribution coefficient.

A.4.3. SYSTEM LAYOUT -- HIGH-PRESSURE METHODS

High-pressure systems are based on the same general apparatus as low-pressure systems (i.e., a fluid reservoir, a fluid delivery system, a column and an effluent collection system) with the inclusion of an extra pressure system that confines the column and pushes solution through the column as illustrated in Figure A-4. Because of the pressures applied (10^2-10^5 psi) on the apparatus, higher strength materials are required, such as Teflon-lined stainless steel. Metal column holders and high-pressure fittings are also needed.

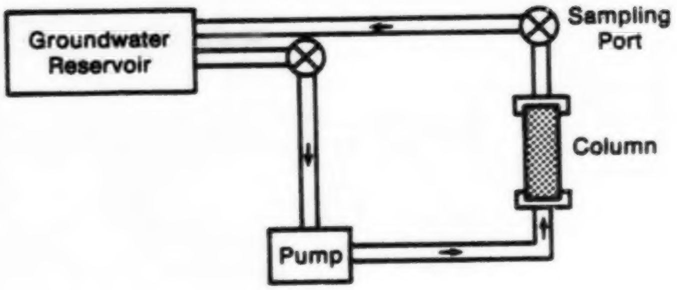
Groundwater Reservoir
Sampling Port
Column
Pump

FIGURE A-3

Apparatus Needed for a Low-Pressure Recirculating Column Retardation Study

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®Registered Trademark of E.I. duPont deNemours and Co., Wilmington, DE.

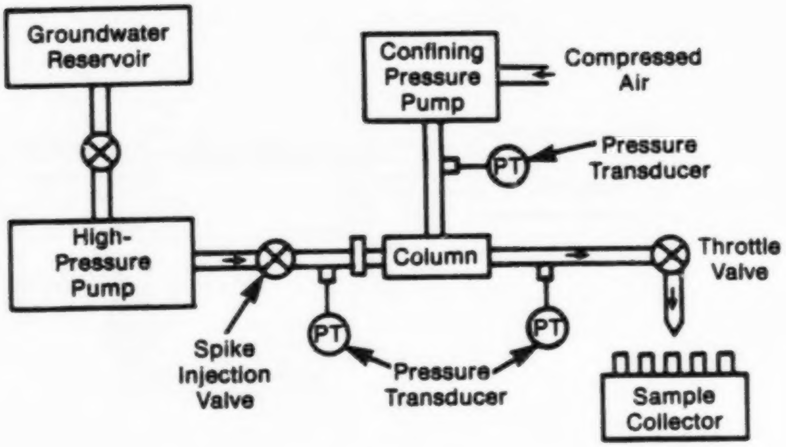
Groundwater Reservoir
Confining Pressure Pump
Compressed Air
PT
Pressure Transducer
High-Pressure Pump
Column
Throttle Valve
PT
PT
Spike Injection Valve
Pressure Transducer
Sample Collector

FIGURE A-4

Apparatus Needed for a High-Pressure Column Retardation Study

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●Registered Trademark of E.I. duPont deNemours and Co., Wilmington, DE.

The influent pump must maintain high pressures to force liquid through low-permeability samples at a relatively constant velocity. The maintenance of a constant velocity is complicated by fluctuations in permeability over time. Constant-flow-rate pumps can accommodate decreases in permeability by increasing the pressure gradient along the column. However, a maximum pressure-setting control is necessary for safety considerations. When that pressure is reached, further declines in permeability will result in decreased groundwater velocity.

High-pressure systems are often applied for rock systems of low permeability. When rock cores are sufficiently impermeable, the groundwater may flow around the core down the edges of the column rather than through the sample. To prevent such short circuiting, the core can be cast in an epoxy jacket that bonds to the rock surface and forms a column wall. Spike injections of contaminant are most commonly employed in high-pressure systems.

A.5. REAGENTS

A.5.1. GROUNDWATER

To the extent possible, groundwater representative of the site of interest should be utilized. If natural groundwaters are not available, they can be synthesized based on key parameters such as total dissolved solids, conductivity, ionic strength, pH, Eh and total organic carbon. Barring the availability of good data, distilled water can be employed to represent meteoric water. Regardless of the source, the water should be analyzed to determine the presence or absence of the contaminant of interest.

Special attention must be directed to maintaining the redox or Eh status of the leaching solution. The solubility of metals is greatly affected by changes in redox potential because of the presence of species couples, such as $S^{-}/SO4^{-2}$, which can produce low-solubility metal salts (i.e., the sulfides). The dissolution and/or evolution of gasses, especially atmospheric oxygen, can greatly affect redox potential. As a consequence, measures should be taken to maintain leaching solutions at the desired redox potential values. Common measures include:

- o Purge oxygen from the air space above leaching solutions by maintaining a nitrogen blanket.
- o Employ a redox buffer in the leaching solution. One such buffer is the pyrogallol-fe^{+2} complex. The concentration of the two species is selected on the basis of the desired Eh level.
- o Prepare the leaching solution fresh daily and monitor Eh before and after use of each batch.

A.5.2. CONTAMINANT

A clean source of the contaminant of interest is required to prepare spikes or continuous-feed solutions. Certified materials should be utilized. Spikes should be prepared as aqueous solutions prior to injection to eliminate problems with solution kinetics. A purity check is advised here. For organics, shelf-life is limited and, therefore, purity checks should be conducted periodically.

A.6. SAMPLE COLLECTION, PRESERVATION AND HOLDING

Samples should be collected serially with a fraction collector or by manual replacement of sample vials at the effluent port. Change-out time should be selected to accumulate a sample volume $\leq$1/20 of a pore volume.

Sample preservation should be done as normally prescribed for the contaminant of interest. If preservatives are indicated, the proper amount should be added to the sample vial and, where necessary, calculations made to account for the added volume of fluid.

Special precautions are required for collection/preservation of volatile contaminants. In the case of cyanides, an alkaline receiving solution in the sample vial can be used to prevent vapor loss. For organic volatiles, direct feed to the analytical instrument or provisions for collection in a closed container are necessary. Holding times should be minimized.

A.7. PROCEDURE

Select the system configuration on the basis of the materials of interest and the availability of apparatus. High-pressure systems are required if low-permeability matrices such as rock cores are to be evaluated.

Assemble the system sizing the column so that diameter is ≥ 30 times the maximum particle diameter and column length is ≥ 4 times column diameter. In all cases, the column volume should be greater than the dead volume (sum of tubing, end-caps, sample-holding screens, etc.).

If an intact core is to be evaluated, the column must be fitted to the core in such a manner that side flow is minimized. For low-permeability cores, an epoxy jacket may be cast around the core. For loose aggregates, the material must be added to the column and packed to a density representative of natural conditions. This can be accomplished mechanically or by repeated pulses with uncontaminated groundwater.

The height of the groundwater reservoir or the pump size/speed should be selected to accomplish the desired groundwater velocity. To reduce the effects of diffusion, select conditions such that:

$$V_{gw} \geq 1.6 \times 10^{-3}/L \text{ cm/sec}$$

where

V_{gw} = groundwater velocity in cm/sec

L = length of the column in cm

Calculate the number of mass transfer units (n) according to:

$$n = \frac{(b)\ (Kd)\ (L)\ (S_k)}{(\theta)\ (V_{gw})} \tag{A-12}$$

where

b = bulk density of the soil/rock matrix (g/cm³)

Kd = distribution coefficient in (µg contaminant/g soil)/(µg contaminant/mℓ groundwater)

L = length of the column in cm

θ = porosity of the soil matrix (dimensionless)

V_{gw} = groundwater velocity in cm/sec

S_k = sorption rate constant (sec^{-1})

to determine if equilibrium is to be expected. In general, 90% of equilibrium is attained when n = 20, while only 50% is reached when n = 3.

If a single-pass system is employed, make up a spike solution such that the concentration approximates contaminant levels of interest and has a total spike volume ≤10% of the total pore volume.

Activate the flow system and observe until flow conditions are steady. Activate the sample collection system. Inject the spike and note the time of injection. Analyze effluent samples and determine the time of passage for the centroid of the peak. Calculate the retardation factor (RF) as:

$$RF = V_{0.5}/\text{effective pore volume} \tag{A-13}$$

where $V_{0.5}$ is the volume eluted when 50% of the total spike has passed (the centroid of the spike).

If a constant-feed system is employed, the feed water should be brought to the desired contaminant concentration and allowed to equilibrate. The system is then activated with the contaminated groundwater feed and the effluent analyzed until the effluent concentration is one-half the influent concentration ($C = 1/2\ C_o$). The volume of eluent at the time $C = 1/2\ C_o$ is defined as $V_{0.5}$ and can be used to calculate RF according to:

$$RF = V_{0.5}/\text{effective pore volume} \tag{A-14}$$

If a recirculating system is employed, the feed groundwater is brought to the desired contaminant concentration and flow initiated. The effluent is monitored until effluent concentrations are equivalent to the influent. At that time, the volume and concentration of eluent are measured to determine the total mass of contaminant adsorbed on the column. This is used to calculate the distribution coefficient (Kd) according to

$$Kd = S/C_f \tag{A-15}$$

where

S = concentration of contaminant on soil/rock (µg/g) or determined by mass of contaminant removed over mass of the soil/rock core

C_f = concentration of feed water

RF is then calculated from Equation A-8.

A.8 CALCULATIONS

Methods for determining the distribution coefficient from column adsorption studies depend on the contact system employed. If a spike feed is utilized, it is necessary to determine when half of the mass of contaminant has passed through the column. This is accomplished through analysis of effluent concentration data. Each sample of effluent is analyzed for the contaminant and results plotted in terms of concentration (vertical axis) and column or pore volumes of effluent (horizontal axis). The spike will appear as a peak in the effluent with width and height determined by the column dimensions, water velocity and attenuation. The area under the peak represents the total mass of contaminant in the effluent. If the peak is symmetrical, the centroid lies at a point directly below the maximum concentration. The cumulative pore volume at that point is defined as $V_{0.5}$, or the volume required for half of the spike to pass from the column. If the peak is not symmetrical, the centroid must be located. The centroid is defined as the vertical line dividing the area under the curve into two equal portions. Once again, the intersection of the vertical line with the horizontal axis defines $V_{0.5}$. The two cases are illustrated in Figure A-5. The retardation factor (RF) is calculated from Equation A-8.

When a constant-feed system is utilized, the plot of concentration and effluent volume represents a breakthrough curve, as illustrated in Figure A-6, rather than a peak. For this system, $V_{0.5}$ is selected as the volume at which effluent concentrations are half of the feed concentrations, or $C/C_o = 0.5$. Once again, Equation A-8 is applied to determine the retardation factor.

Once the value for RF has been determined, the distribution coefficient (Kd) can be calculated from the conversion of Equation A-8:

$$Kd = (RF - 1)/\theta/b \qquad \text{(A-16)}$$

where

θ = porosity of the soil column (dimensionless)

b = bulk density of the soil in the column (g/cm^3)

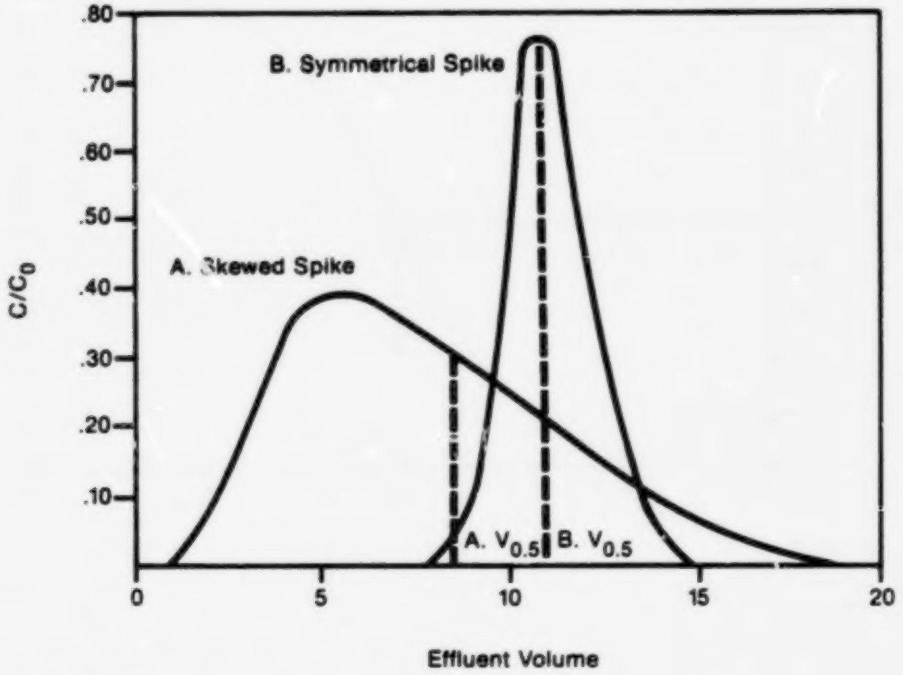


FIGURE A-5

Selection of $V_{0.5}$ from Spike Elution Data

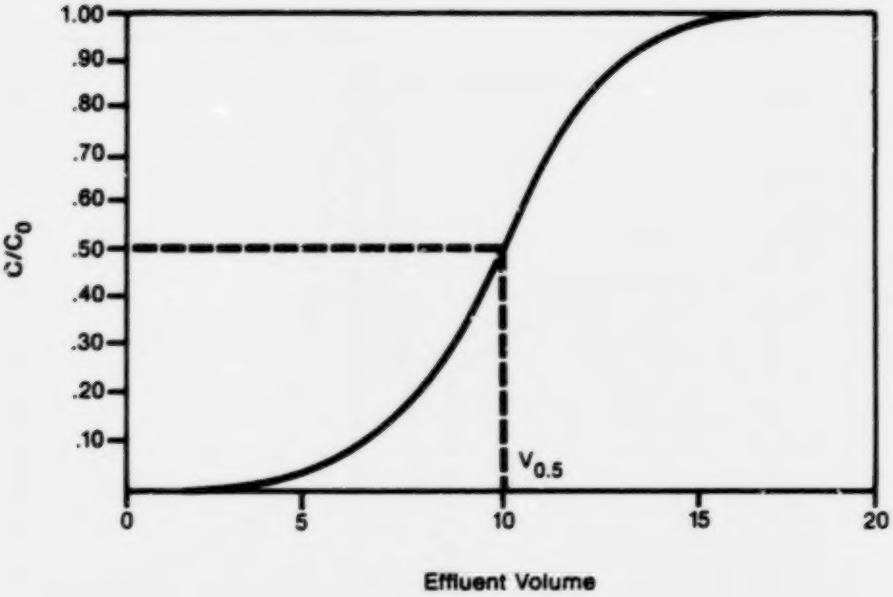


FIGURE A-6

Selection of $V_{0.5}$ from Continuous-Feed Data

If a recirculating system is employed, Kd can be determined directly. The influent and effluent lines are analyzed continuously for the contaminant of interest, and the eluent volume is monitored. The concentration and volume are recorded at the time when influent and effluent concentrations are equivalent. The total mass of contaminant (M_T) in the system is defined as:

$$M_T = V_w C_o \tag{A-16}$$

where

V_w = total volume of solution in the apparatus (ℓ)

C_o = initial concentration of contaminant in the solution (mg/ℓ)

The mass of dissolved contaminant (M_S) at the end of the procedure is defined as:

$$M_S = V_w C_f \tag{A-18}$$

where C_f = final concentration of contaminant in solution (mg/ℓ).

Therefore, the absorbed mass of contaminant (Ma) is defined as:

$$Ma = M_T - M_S \tag{A-19a}$$

$$= V_w (C_o - C_f) \tag{A-19b}$$

The concentration of contaminant on the soil (S) is calculated as:

$$S = Ma/W \tag{A-20}$$

where W = mass of soil in the column (Kg).

$$W = V_s (b/\theta) \tag{A-21}$$

where

Vs = volume of soil in the column (cm^3)

b = bulk density of the soil in the column (g/cm^3)

θ = porosity of the soil in the column (dimensionless)

Combining Equations A-18, A-19b, A-20 and A-21, the distribution coefficient (Kd) is calculated as:

$$Kd = (V_w/V_s)[C_o - C_f)/C_f]/(b/\theta) \qquad (A\text{-}22)$$

A.9. REFERENCES

Material in this appendix is derived from the following references:

Relyea, J.F. 1981. Status report: Column method for determining retardation factors. U.S. Dept. of Energy, Richland, WA. PNL-4031, UC-70.

Relyea, J.F. 1982. Theoretical and experimental considerations for the use of the column method for determining retardation factors. Radioactive Waste Management and the Nuclear Fuel Cycle. 3: 151-156. (Modified)

APPENDIX B

INPUT PARAMETERS FOR CONTAMINANTS OF INTEREST

B.1. DISTRIBUTION COEFFICIENTS

Distribution coefficients are required to determine how a contaminant will partition itself between the soil particles and the soil water. The distribution coefficient (Kd) is defined as:

$$Kd = S/C \tag{B-1}$$

where

S = concentration of contaminant on soil (mg/kg)

C = concentration of contaminant in water (mg/ℓ)

The concept of Kd is a gross simplification of attenuation of inorganic contaminants in soil. Precipitation chemistry is an important factor in attenuation over and above adsorption and exchange. Precipitation does not yield a solution concentration in proportion to the mass of contaminant in the system. As a consequence, the use of a Kd is most valid at low contaminant concentration levels where contaminants do not exceed solubility thresholds.

For organics, the Kd concept is more broadly useful because adsorption accounts for most soil attenuation. In the case of organics, Kd is calculated from the distribution as a function of organic carbon content of the soil (K_{oc}) and the fraction of soil (f_{oc}) consisting of organic matter as follows:

$$Kd = (K_{oc})(f_{oc}) \tag{B-2}$$

If values for K_{oc} have not been determined experimentally, equations are available that relate K_{oc} to octanol/water partition coefficient data -- (K_{ow}) or solubility.

Table B-1 is provided to assist the analyst in selecting Kd values for contaminants of interest. Values for inorganic contaminants were derived

TABLE B-1

Distribution Coefficients for Selected Contaminants

Contaminant	Koc [(mg/kg_{oc})/(mg/ℓ)] (organics only)	Soil Type	Kd - Distribution Coefficient [(mg/kg)/(mg/ℓ)] Unsaturated Sand	Unsaturated Sandy Loam	Unsaturated Silty Loam	Unsaturated Silty Clay Loam	Saturated Sand	Saturated Sandy Loam	Reference
		Organic Fraction	0.0001	0.005	0.001	0.13	0.0	0.0	
Aldrin	4.6×10^3		0.46	23	4.6	59	0.0	0.0	Dawson et al., 1980
Arsenic	NA		5.86	19.4			5.86	19.4	U.S. EPA, 1985a
Benzene	74		7.4×10^{-3}	0.37	7.4×10^2	0.96	0.0	0.0	U.S. EPA, 1985a
Benzo(a)anthracene	1.38×10^6		138	6900	1380	1.8×10^4	0.0	0.0	Lyman et al., 1982
Benzo(a)pyrene	6.3×10^5		63	3.2×10^{22}	630	8.2×10^3	0.0	0.0	U.S. EPA, 1985a
Bis (2 ethyl hexyl) pthalate	7244		0.72	36	7.2	94	0.0	0.0	U.S. EPA, 1985a
Cadmium	NA		14.9	423			14.9	423	U.S. EPA, 1985a
Carbon Tetrachloride	650		0.065	3.25	0.65	84.5	0.0	0.0	U.S. EPA, 1985a
Chlordane	1.7×10^5		17	850	170	2.2×10^3	0.0	0.0	U.S. EPA, 1985a
Chloroform	280		0.028	1.4	0.28	36.4	0.0	0.0	U.S. EPA, 1985a
Chromium	NA		16.8	56.5			16.8	56.5	U.S. EPA, 1985a
Cobalt	NA		1.94	8.81			1.94	8.81	U.S. EPA, 1985a
Copper	NA		41.9	92.2			0.0	92.2	U.S. EPA, 1985a
Cyanide	NA		0.0	0.0			0.0	0.0	U.S. EPA, 1985a

TABLE B-1 (cont.)

Contaminant	K_{oc} [(mg/kg$_{oc}$)/(mg/ℓ)] (organics only)	Kd - Distribution Coefficient [(mg/kg)/(mg/ℓ)]							Reference
		Soil Type	Unsaturated Sand	Unsaturated Sandy Loam	Unsaturated Silty Loam	Unsaturated Silty Clay Loam	Saturated Sand	Saturated Sandy Loam	
		Organic Fraction	0.0001	0.005	0.001	0.13	0.0	0.0	
DDT/DDE/DDD	5×10^6		500	2.5×10^4	5×10^3	6.5×10^4	0.0	0.0	U.S. EPA, 1985a
2,4-Dichlorophenoxyacetic acid	20		2×10^{-3}	0.1	2×10^{-2}	0.26	0.0	0.0	Dawson et al., 1980
Dieldrin	908		9.1×10^{-1}	4.5	9.1×10^{-1}	12	0.0	0.0	Dawson et al., 1980
Dimethylnitrosamine	0.04		4×10^{-6}	2×10^{-4}	4×10^{-5}	5.2×10^{-3}	0.0	0.0	U.S. EPA, 1985a
Fluoride	NA		0.0	0.0	0.0	0.0	0.0	0.0	Estimate based on solubility of fluoride salts
Heptachlor	3164		0.3	46	3	39	0.0	0.0	Dawson et al., 1980
Hexachlorobenzene	3900		0.4	20	4	52	0.0	0.0	Dawson et al., 1980
Hexachlorobutadiene	7595		0.8	38	8	104	0.0	0.0	Dawson et al., 1980
Iron	NA		15				15		O'Melia and Strumm, 1967
Lead	NA		234	597			234	597	U.S. EPA, 1985a
Lindane	1080		0.1	5.4	1.0	1.3	0.0	0.0	U.S. EPA, 1985a
Malathion	1800		0.18	9.0	1.8	2.3	0.0	0.0	U.S. EPA, 1985a
Mercury	NA		322	580			322	580	U.S. EPA, 1985a

TABLE B-1 (cont.)

Contaminant	K_{oc} [(mg/kg_{oc})/(mg/ℓ)] (organics only)	Kd - Distribution Coefficient [(mg/kg)/(mg/ℓ)]							Reference
		Soil Type	Unsaturated Sand	Unsaturated Sandy Loam	Unsaturated Silty Loam	Unsaturated Silty Clay Loam	Saturated Sand	Saturated Sandy Loam	
		Organic Fraction	0.0001	0.005	0.001	0.13	0.0	0.0	
Methylene bis (2-chloroaniline)	9120		0.91	46	9.1	120	0.0	0.0	U.S. EPA, 1985b
Methylene chloride	10		1×10^{-3}	5×10^{-2}	1×10^{-2}	0.13	0.0	0.0	U.S. EPA, 1985a
Methyl ethyl ketone	24		3.4×10^{-3}	0.17	3.4×10^{-2}	0.44	0.0	0.0	U.S. EPA, 1985b
Molybdenum	NA		8.58	43.4			8.58	43.4	U.S. EPA, 1985a
Nickel	NA		12.2	58.6			12.2	58.6	U.S. EPA, 1985a
Nitrate	NA		0.0	0.0	0.0	0.0	0.0	0.0	Estimate based on solubility of nitrate salts
Pentachlorophenol	1.26×10^{4}		1.26	63	13	169	0.0	0.0	Dawson et al., 1980
Phenanthrene	2.3×10^{4}		2.3	115	23	300	0.0	0.0	U.S. EPA, 1985a
Phenol	16.6		1.6×10^{-3}	0.08	1.6×10^{-2}	0.22	0.0	0.0	U.S. EPA, 1985a
Polychlorinated biphenyls	3.2×10^{6}		320	1.6×10^{3}	3.2×10^{3}	4.2×10^{4}	0.0	0.0	U.S. EPA, 1985a
Selenium	NA		5.91	14.9			5.91	14.9	U.S. EPA, 1985a
Tetrachloroethylene	618		0.062	3.1	0.62	80	0.0	0.0	U.S. EPA, 1985a
Toxaphene	960		9.6×10^{-2}	4.82	0.96	12	0.0	0.0	U.S. EPA, 1985a

TABLE B-1 (cont.)

		Kd - Distribution Coefficient [(mg/kg)/(mg/ℓ)]							
Contaminant	K_{oc} [(mg/kg_{oc})/(mg/ℓ)] (organics only)	Soil Type	Unsaturated Sand	Unsaturated Sandy Loam	Unsaturated Silty Loam	Unsaturated Silty Clay Loam	Saturated Sand	Saturated Sandy Loam	Reference
		Organic Fraction	0.0001	0.005	0.001	0.13	0.0	0.0	
Trichloroethylene	198		2.0×10^{-2}	0.99	0.2	2.6	0.0	0.0	U.S. EPA, 1985a
Tricresyl Phosphate	840		0.08	4.2	0.8	10	0.0	0.0	Lyman et al., 1982
Vinyl Chloride	134		0.013	0.65	0.13	17	0.0	0.0	U.S. EPA, 1985a
Zinc	NA		12.7	939			12.7	939	U.S. EPA, 1985a

NA = Not applicable

from the literature for sandy and sandy-loam soils. No difference is anticipated between unsaturated and saturated soils. The analyst should select the soil condition most closely matched to soils found on the site for selection of the Kd.

For organic contaminants, the Kd is a function of organic content in soil. As a consequence, the analyst has two options:

1. If the organic content of the soil on the site is known, the K_{OC} value should be selected from Table B-1 and the Kd calculated from Equation B-2.
2. If the organic content of the soil on the site is not known, the soil classification should be matched with those soil types provided in Table B-1 and the associated Kd value selected.

It is assumed that subsoils in the aquifer will not have organic matter and, therefore, the Kd for organics in the saturated zone is equated to zero. This is conservative in that research suggests that at low organic levels (i.e., <0.1%), organics interact with clay minerals. However, these interactions are not well understood and no means of prediction is currently available. Therefore, retention in the saturated zone is not considered at this time.

Whenever specific Kd values are available for the on-site soil, they should be employed in place of the values provided in Table B-1. Use of such data should be accompanied by detailed documentation on how they were derived.

B.2. HENRY'S LAW CONSTANTS

The Henry's Law Constant allows one to calculate vapor concentrations over a solution as a function of the contaminant's concentration in the solution. If Henry's Law Constants (H) have not been derived experimentally, they are estimated according to:

$$H + P_{vp}/S \qquad \text{(B-3)}$$

where

P_{vp} = vapor pressure of contaminant (atm)

S = solubility of contaminant in water (mol/m^3)

Both S and P_{vp} need to be measured at the same temperature. Hence, if vapor pressures are given at a different temperature, they must be adjusted. The Henry's Law Constant can also be determined from thermodynamic data describing the free energy of solution if such data are available. This approach considers the reaction for dissolution of a gas:

$$A(l) = A(g) \qquad \text{(B-4)}$$

The equilibrium constant for the above reaction is:

$$Ks = \frac{\{A(g)\}}{\{A(l)\}} \qquad \text{(B-5)}$$

where {A(g)} is the activity of constituent A in the atmosphere and {A(l)} is the activity in solution. By definition, the activity in the atmosphere is equal to the partial pressure and the activity in solution is equal to the concentration in solution, multiplied times an activity coefficient. Equation B-5 can then be rewritten as:

$$Ks = \frac{P_A}{[A(l)]\gamma A} \qquad \text{(B-6)}$$

where

P_A = partial pressure of constituent A (atm)

$[A(l)]$ = concentration of A in solution (M/ℓ)

γ_A = activity coefficient of A (dimensionless)

Because $P_A/[A(l)]$ is the Henry's Law Constant, Equation B-6 can be rewritten as:

$$H = Ks\ \gamma_A \qquad \text{(B-7)}$$

TABLE B-2

Activity Coefficients for Species of Various Charge for Various Ionic Strengths

I (M/ℓ)	γ_0[a]	$\gamma_{\pm 1}$[b]	$\gamma_{\pm 2}$[c]
0.01	1.00	0.901	0.658
0.02	1.00	0.867	0.565
0.03	1.01	0.844	0.507
0.04	1.01	0.825	0.464
0.05	1.01	0.810	0.431
0.06	1.01	0.797	0.404
0.07	1.02	0.786	0.382
0.08	1.02	0.776	0.362
0.09	1.02	0.767	0.346
0.10	1.02	0.776	0.363
0.12	1.03	0.764	0.325
0.14	1.03	0.755	0.324
0.16	1.04	0.747	0.311
0.18	1.04	0.740	0.299
0.20	1.05	0.734	0.290
0.22	1.05	0.728	0.281
0.24	1.06	0.724	0.274
0.26	1.06	0.720	0.268
0.28	1.07	0.716	0.263
0.30	1.07	0.713	0.258
0.32	1.08	0.710	0.254

TABLE B-2 (cont.)

I (M/ℓ)	$\gamma 0$[a]	$\gamma \pm 1$[b]	$\gamma \pm 2$[c]
0.34	1.08	0.708	0.251
0.36	1.09	0.706	0.248
0.38	1.09	0.704	0.245
0.40	1.10	0.702	0.243
0.42	1.10	0.700	0.241
0.44	1.11	0.699	0.239
0.46	1.11	0.698	0.238
0.48	1.12	0.697	0.236
0.50	1.12	0.696	0.235

[a] $\gamma 0$ = Activity coefficient of uncharged species

[b] $\gamma \pm 1$ = Activity coefficient of singly charged species

[c] $\gamma \pm 2$ = Activity coefficient of doubly charged species

The activity coefficient depends on the ionic strength of the solution. Representative values are given in Table B-2.

The equilibrium constant, Ks, can be calculated from the free energy of reaction B-4:

$$Ks = e^{-\Delta°F/RT} \qquad \text{(B-8)}$$

where

$\Delta°F$ = free energy of the reaction (cal/mol)

R = Universal Gas Law Constant (cal/mol-°K)

T = absolute temperature (°K)

The free energy of the reaction is defined as the difference in the free energy of formation of the gas and dissolved constituent:

$$\Delta°F = °F_f(g) - °F_f(\ell) \qquad \text{(B-9)}$$

where

$°F_f(g)$ = standard free energy of formation of the gaseous constituent

$°F_f(\ell)$ = standard free energy of formation of the liquid constituent

Standard free energy of formation data are tabulated in the Handbook of Chemistry and Physics, published annually by the Chemical Rubber Company.

The value of H thus derived is in units of atm-mol/m^3, which is not an easy one to work with. Most analysts prefer to use a modified Henry's Law Constant (H') that is dimensionless. The modified constant is derived as:

$$H' = \frac{(1.0135\text{x}10^5)H}{R\ T} \qquad \text{(B-10)}$$

where

$1.0135\text{x}10^{-5}$ = conversion constant (N/m^2-atm)

H = Henry's Law Constant (atm-m^3/mol)

R = Universal Gas Law Constant (8.315 N-m/mol -°K)

T = temperature (°K = C + 273)

For charged species and $0.1 < I < 0.5$:

$$-\log\gamma = 0.5\ Z^2\ \left(\frac{\sqrt{I}}{\sqrt{1} + I} - 0.2I\right) \qquad \text{(Butler, 1964)}$$

For unchanged species

$$\log \gamma_0 = KI$$

where K is a constant. Unless otherwise given, K = 0.10 as suggested by Butler (1964).

Values for H and H' were found in the literature or derived for the contaminants of interest and are listed in Table B-3. The references indicate where the values or the inputs for derivation of values were obtained. The notes specify the method of derivation when published values were not found.

B.3. POROUS MEDIA HYDROLOGIC PROPERTIES

The methodology for evaluating disposal of municipal sewage sludges requires the input of various site-specific values related to hydrologic flow in soils and other geologic media. Some of these values must be determined by direct measurement, while others can be selected from reported values for given soil types or aquifer media. The following tables and figures present typical values to assist the applicant and/or reviewer in determining the reasonableness of values derived for specific applications:

- Table B-4 provides typical values for the slope of the moisture retention curve for soils that may be found in the unsaturated zone.
- Figure B-1 provides ranges of values for saturated hydraulic conductivity of different aquifer media.
- Table B-5 provides ranges of values for porosity of unsaturated and saturated zone media.

TABLE B-3

Henry's Law Constants (H) and Dimensionless Henry's Law Constants (H') (Assumed Temperature: 20°C)[a] for Selected Contaminants

Contaminant	H (atm-m^3/mol)	H' (Dimensionless)	Reference
Aldrin	1.4×10^{-5}	6.1×10^{-4}	Lyman et al., 1982
Arsenic	NV	NV	
Benzene	5.5×10^{-3}	2.4×10^{-1}	Lyman et al., 1982
Benzo(a)anthracene	NV	NV	U.S. EPA, 1985a[b]
Benzo(a)pyrene	NV	NV	
Bis(2-ethylhexyl) phthalate	1.0	40	U.S. EPA, 1985a[b]
Carbon tetrachloride	2.3×10^{-2}	9.7×10^{-1}	Lyman et al., 1982
Cadmium	NV	NV	
Chlordane	0.59	24	U.S. EPA, 1985a[b]
Chloroform	4.8×10^{-3}	2.0×10^{-1}	Lyman et al., 1982
Chromium	NV	NV	
Cobalt	NV	NV	
Copper	NV	NV	
Cyanide	1.9×10^{-3}	0.082	c/ for 10°C
DDT/DDE/DDD	3.8×10^{-5}	1.7×10^{-3}	Lyman et al., 1980
2,4-Dichlorophenoxy-acetic acid	9×10^{-5}	3.7×10^{-3}	Dawson et al., 1980[b]
Dieldrin	2×10^{-7}	8.9×10^{-6}	Lyman et al., 1982
Dimethylnitrosamine	4.9×10^{-4}	2.0×10^{-2}	Dawson et al., 1980[b]
Fluoride	(pH = 6): 1×10^{-7} (pH = 7): 1×10^{-8}	(pH = 6): 4.4×10^{-6} (pH = 7): 4.4×10^{-7}	c/ for 10°C

TABLE B-3 (cont.)

Contaminant	H (atm-m^3/mol)	H' (Dimensionless)	Reference
Heptachlor	7×10^{-5}	2.9×10^{-3}	Dawson et al., 1980[b]
Hexachlorobenzene	3.7×10^{-5}	1.5×10^{-3}	U.S. EPA, 1985a[b]
Hexachlorobutadiene	3.73	122	Verschueren, 1983[b]
Iron	NV	NV	
Lead	NV	NV	
Lindane	4.8×10^{-7}	2.2×10^{-5}	Lyman et al., 1982
Malathion	1.2×10^{-7}	5×10^{-6}	Dawson et al., 1980[b]
Mercury	1.1×10^{-2}	4.8×10^{-1}	Lyman et al., 1982
Methylene bis (2-chloroaniline)	5.1×10^{-7}	2.1×10^{-6}	U.S. EPA, 1985a[b]; SRI, 1984[b]
Methylene chloride	3×10^{-3}	1.3×10^{-1}	Lyman et al., 1982
Methyl ethyl ketone	20.8	900	U.S. EPA, 1985a[b]
Molybdenum	NV	NV	
Nickel	NV	NV	
Nitrate	NV	NV	
Pentachlorophenol	3.4×10^{-6}	1.5×10^{-4}	Lyman et al., 1982
Phenanthrene	3.9×10^{-5}	1.7×10^{-3}	Lyman et al., 1982
Phenol	3×10^{-7}	1.2×10^{-5}	U.S. EPA, 1985a[b]
Polychlorinated biphenyls:			
Aroclor 1242	5.6×10^{-4}	2.4×10^{-2}	Lyman et al., 1982
Aroclor 1254	2.7×10^{-3}	1.2×10^{-1}	Lyman et al., 1982
Aroclor 1248	3.5×10^{-3}	1.6×10^{-1}	Lyman et al., 1982
Aroclor 1260	7.1×10^{-3}	3.0×10^{-1}	Lyman et al., 1982
Selenium	NV	NV	

TABLE B-3 (cont.)

Contaminant	H (atm-m^3/mol)	H' (Dimensionless)	Reference
Tetrachloroethylene	8.3×10^{-3}	3.4×10^{-1}	Lyman et al., 1982
Toxaphene	5.4×10^{-2}	2.2	Dawson et al., 1980[b]
Trichloroethylene	1×10^{-2}	4.2×10^{-1}	Lyman et al., 1982
Tricresyl phosphate	1.5×10^{-2}	0.61	MSDS[b]
Vinyl chloride	2.4	99	Lyman et al., 1982
Zinc	NV	NV	

[a] The dimensionless Henry's Law Constant can be estimated by (Thibodeaux, 1979):

$$H' = \frac{16\ P_v\ (MW)}{(SOL)\ T}$$

where

H' = Henry's Law Constant (cm^3/cm^3)
P_v = saturation vapor pressure of the contaminant (mm Hg)
(MW) = molecular weight of the compound (g/g mol)
SOL = contaminant's solubility in water (ppm)
T = ambient temperature (°K)

[b] Henry's Law Constant (H) calculated from Equation B-3; dimensionless Constant (H') calculated from B-5

[c] Henry's Law Constant (H) calculated Equation B-4; dimensionless Constant (H') calculated from Equation B-5

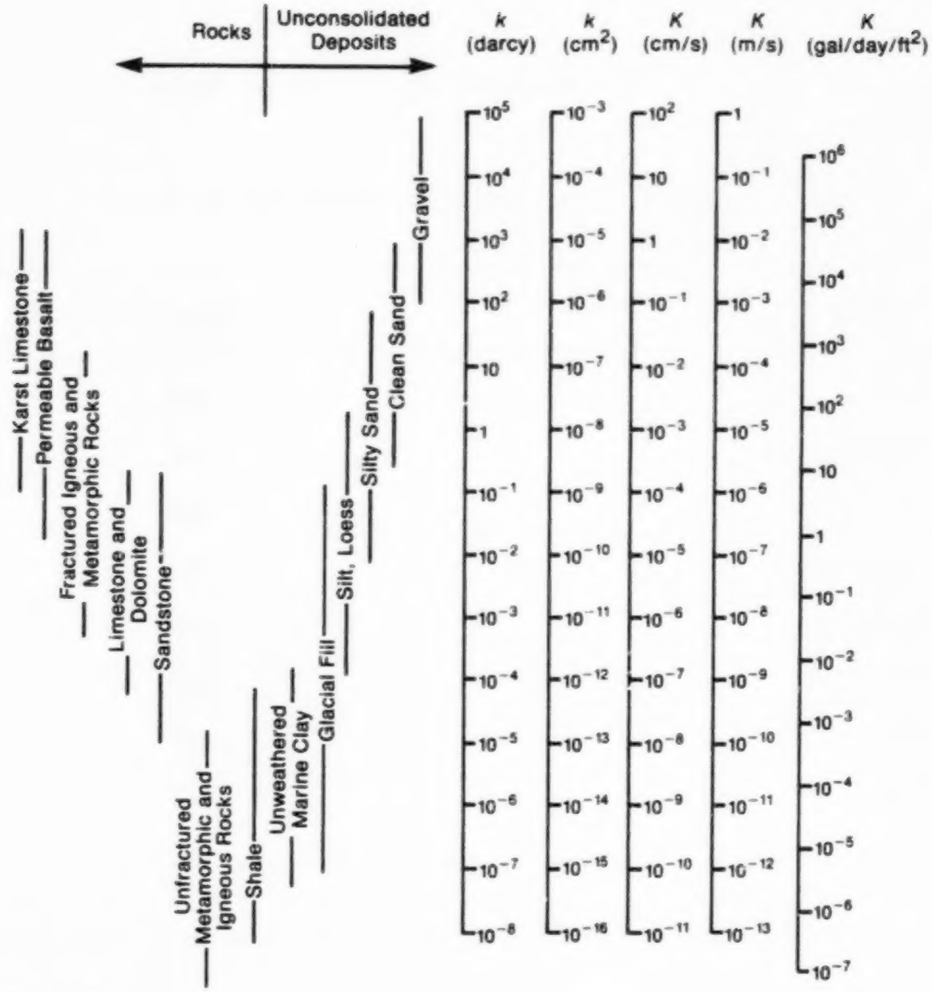
NV = A calculation of Henry's Law Constants for these materials is not meaningful. No measurable vapor levels are anticipated.

TABLE B-4

Typical Values for Slope of Soil Moisture Retention Curve*

Soil Texture	Value for Curve (b)
Clay	11.7
Silty clay	9.9
Silty clay loam	7.5
Clay loam	8.5
Sandy clay loam	7.5
Sandy silt loam	5.4
Silty loam	4.8
Sandy loam	6.3
Loamy sand	5.6
Sand	4.0

*Source: Hall et al., 1977



Conversion Factors

	Permeability, *k**			Hydraulic conductivity, *K*		
	cm^2	ft^2	darcy	m/s	ft/s	gal/day/ft^2
cm^2	1	1.08×10^{-3}	1.01×10^{8}	9.80×10^{2}	3.22×10^{3}	1.85×10^{9}
ft^2	9.29×10^{2}	1	9.42×10^{10}	9.11×10^{5}	2.99×10^{6}	1.71×10^{12}
darcy	9.87×10^{-9}	1.06×10^{-11}	1	9.66×10^{-6}	3.17×10^{-5}	1.82×10^{1}
m/s	1.02×10^{-3}	1.10×10^{-6}	1.04×10^{5}	1	3.28	2.12×10^{6}
ft/s	3.11×10^{-4}	3.35×10^{-7}	3.15×10^{4}	3.05×10^{-1}	1	5.74×10^{5}
gal/day/ft^2	5.42×10^{-10}	5.83×10^{-13}	5.49×10^{-2}	4.72×10^{-7}	1.74×10^{-6}	1

*To obtain *k* in ft^2, multiply *k* in cm^2 by 1.08×10^{-3}.

FIGURE B-1

Representative Values for Saturated Hydraulic Conductivity

Source: Freeze and Cherry, 1979

TABLE B-5

Porosity Values for Porous Media

A. Representative Values for Porosity

Material	Porosity
Coarse gravel	28%
Medium gravel	32%
Fine gravel	34%
Coarse sand	39%
Medium sand	39%
Fine sand	43%
Silt	46%
Clay	42%

B. Effective Porosities for General Hydrogeologic Classifications*

Generic Classification	Effective Porosity (Dimensionless)
Fractured Crystalline Silicates	0.01
Fractured and Solutioned Carbonates	0.10
Porous Carbonates	0.10
Porous Silicates	0.01
Porous Unconsolidated Silicates	Average Value 0.16
Fractured Shale	0.01

*Source: Shafer et al., 1984

B.4. GEOCHEMICAL CONSIDERATIONS

The following series of figures are provided to convert unsaturated zone contaminant concentrations to resulting saturated zone concentrations based on geochemical interactions. Each figure addresses a specific inorganic contaminant (arsenic, 3.1; mercury, 3.2; lead, 3.3; copper, 3.4; and nickel, 3.5). Six curves are provided for each contaminant (a-f) depicting relations for a different set of pH and Eh conditions. The pH values included are 6.0 and 7.0. Eh values are -200 mv, +150 mv and +500 mv. Directions for use of the curves can be found in Section 4.3.3.1.

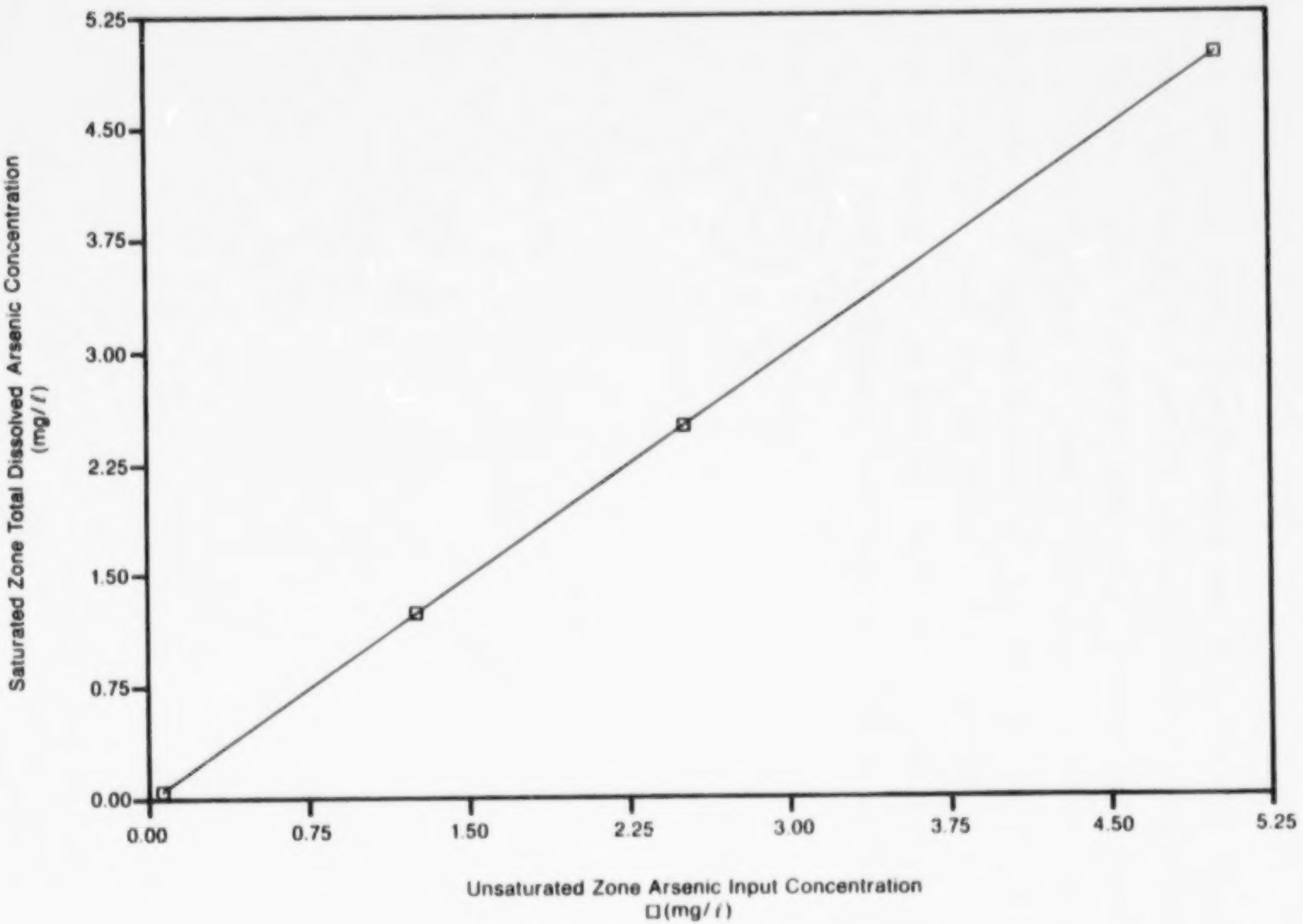


FIGURE B-2a

Saturated Zone Arsenic Concentration after Speciation

Conditions: pH = 7.0, Redox = 500 mv

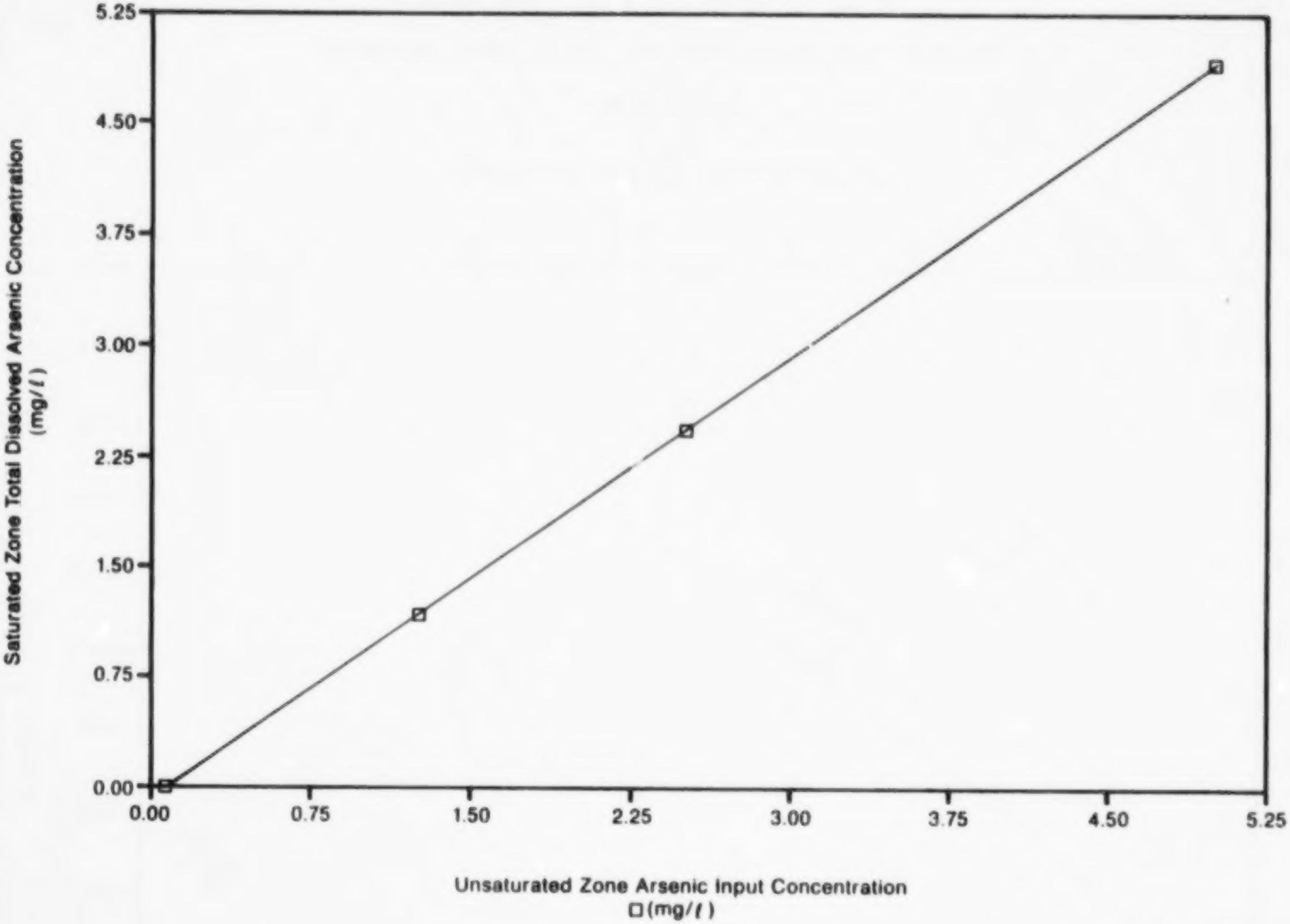


FIGURE B-2b

Saturated Zone Arsenic Concentration after Speciation

Conditions: pH = 7.0, Redox = 150 mv

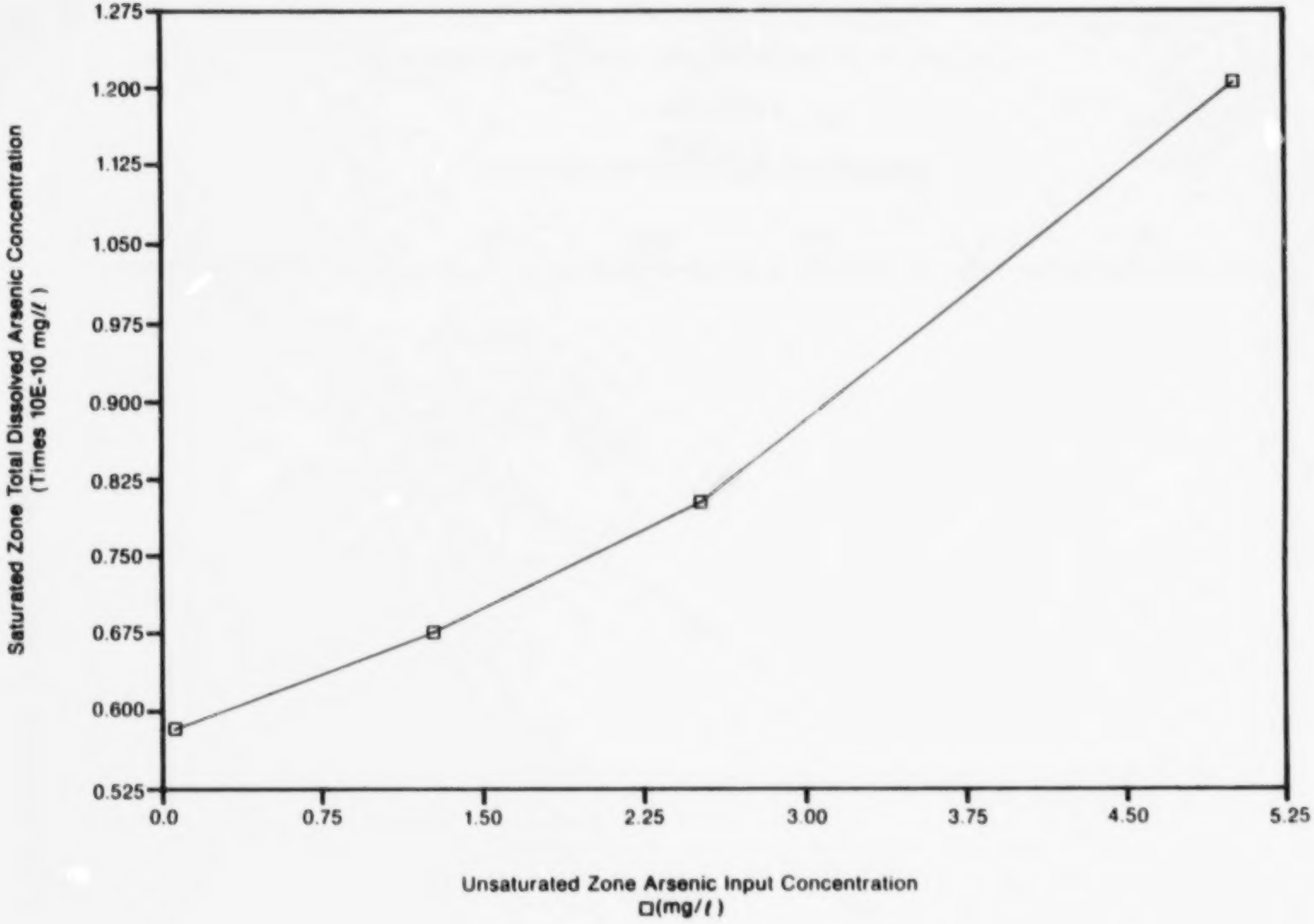


FIGURE B-2c

Saturated Zone Arsenic Concentration after Speciation

Conditions: pH = 7.0, Redox = -200 mv

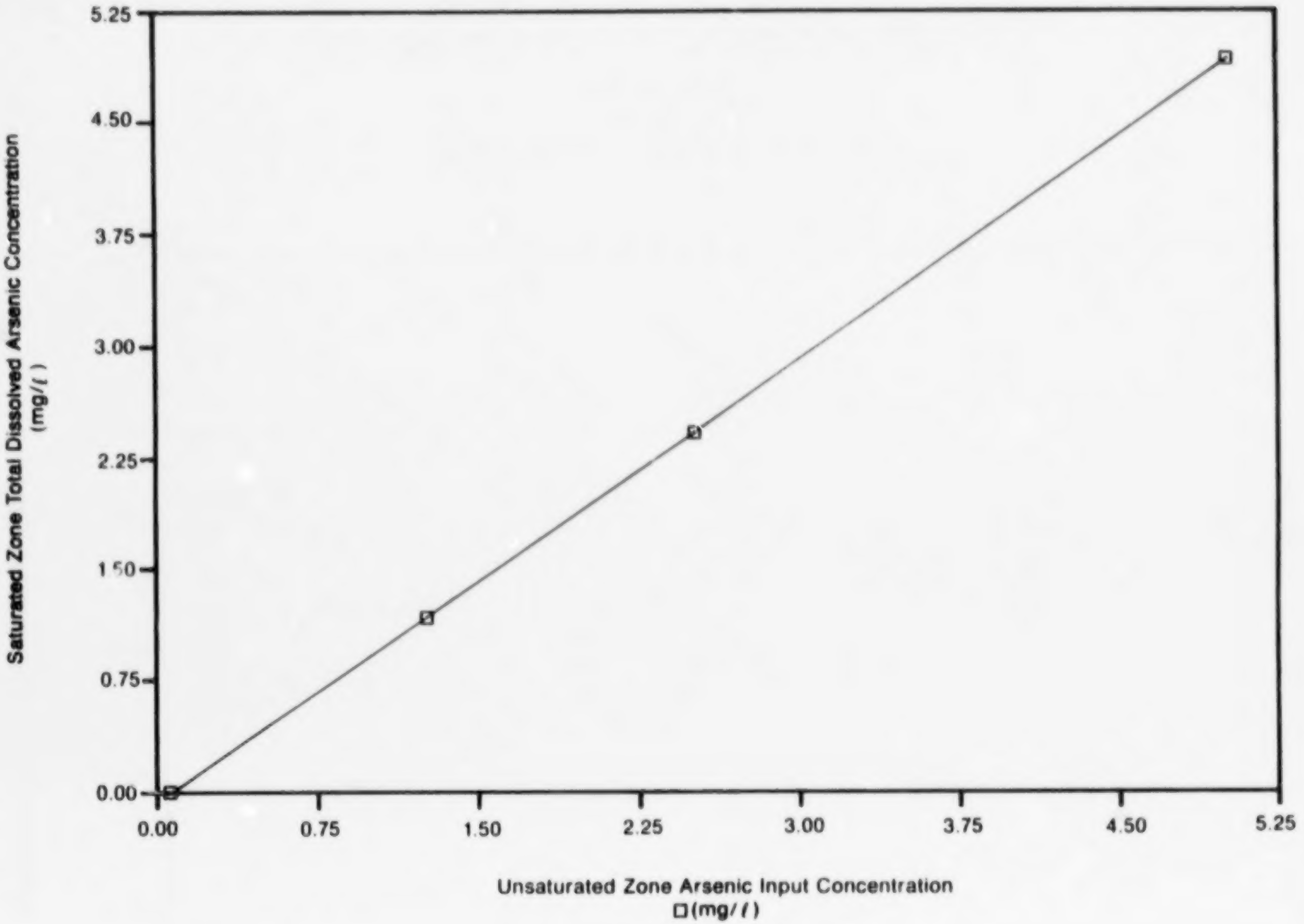


FIGURE B-2d

Saturated Zone Arsenic Concentration after Speciation

Conditions: pH = 6.0, Redox = 500 mv

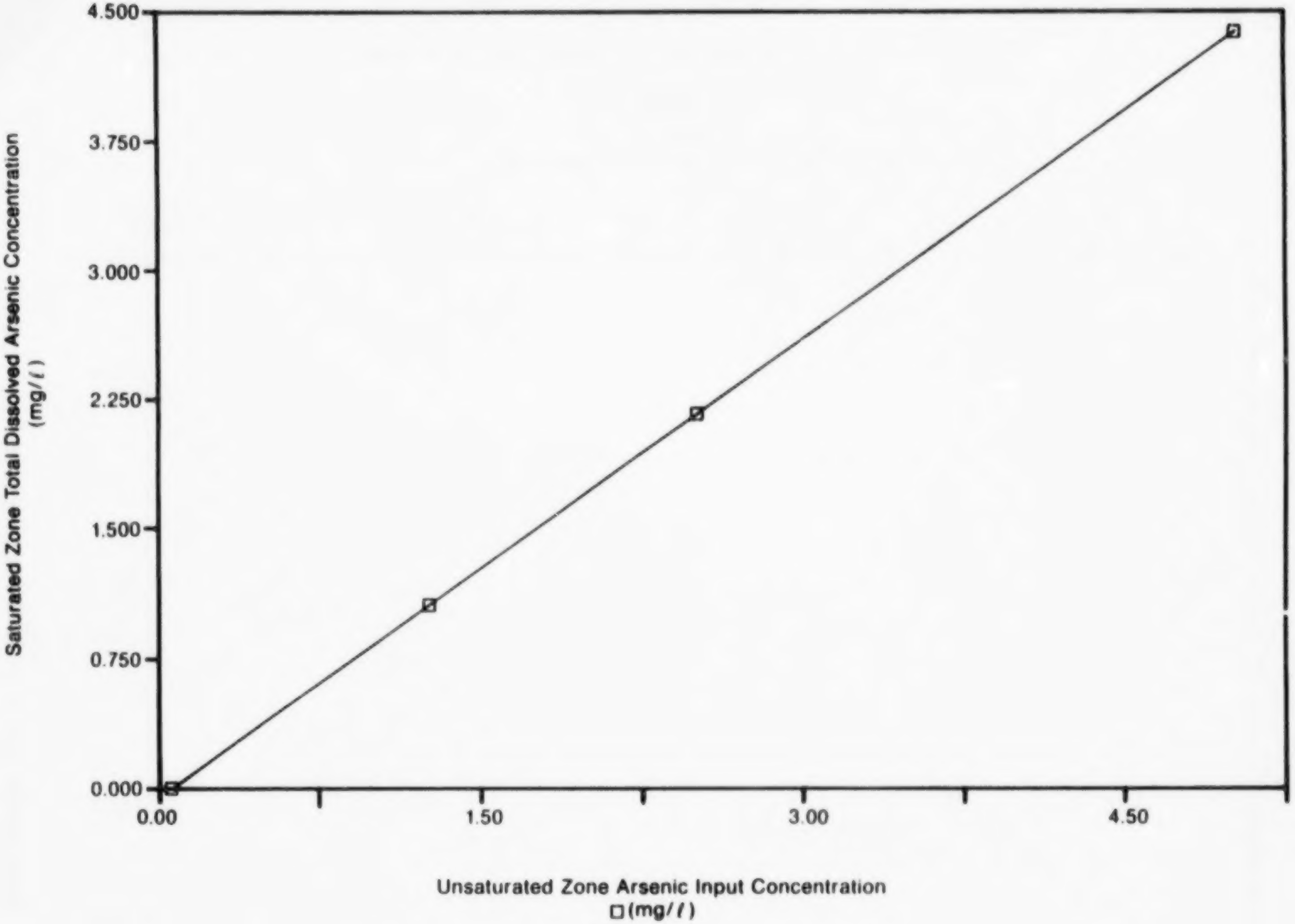


FIGURE B-2e

Saturated Zone Arsenic Concentration after Speciation

Conditions: pH = 6.0, Eh = 150 mv

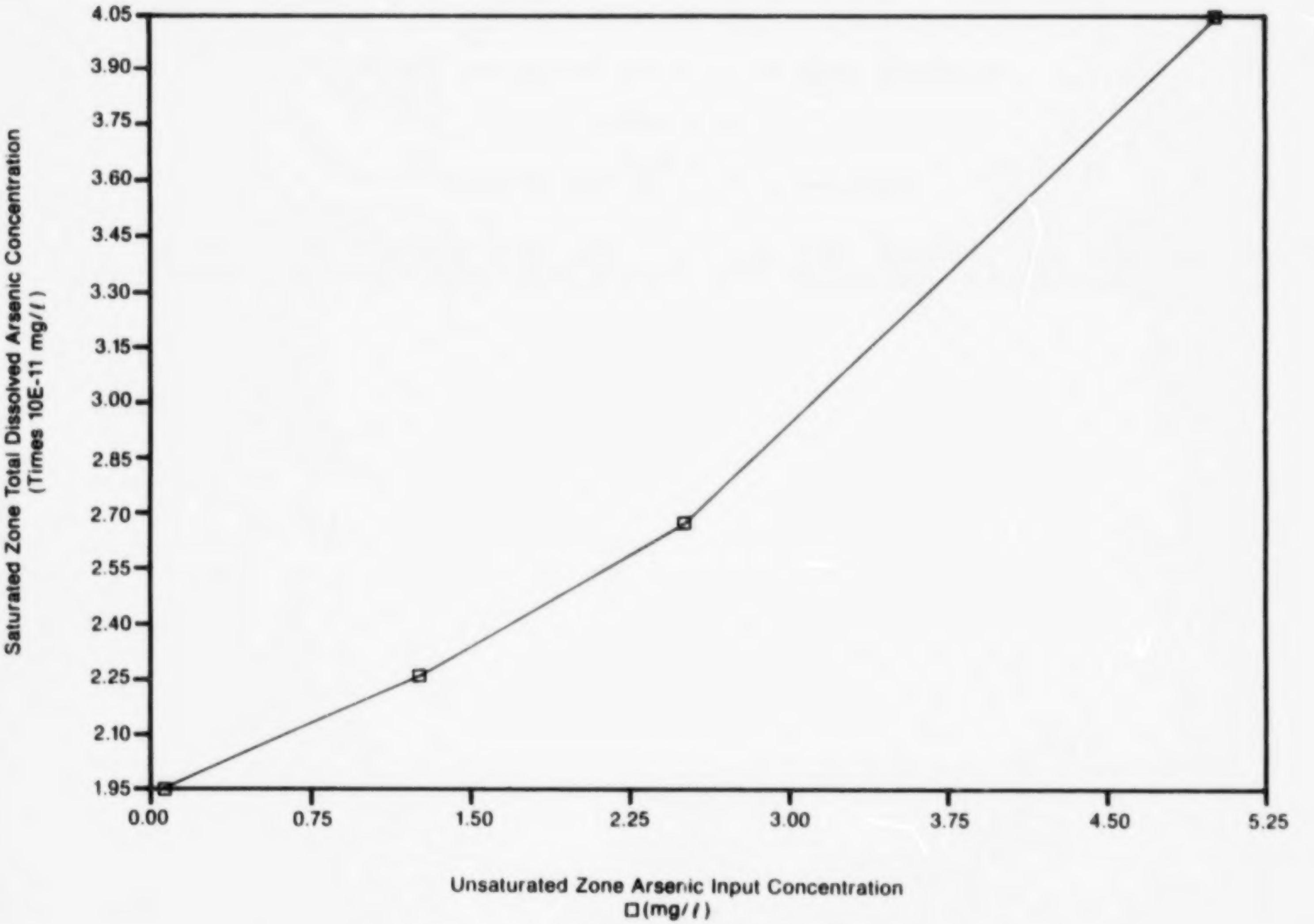


FIGURE B-2f

Saturated Zone Arsenic Concentration after Speciation

Conditions: pH = 6.0, Redox = -200 mv

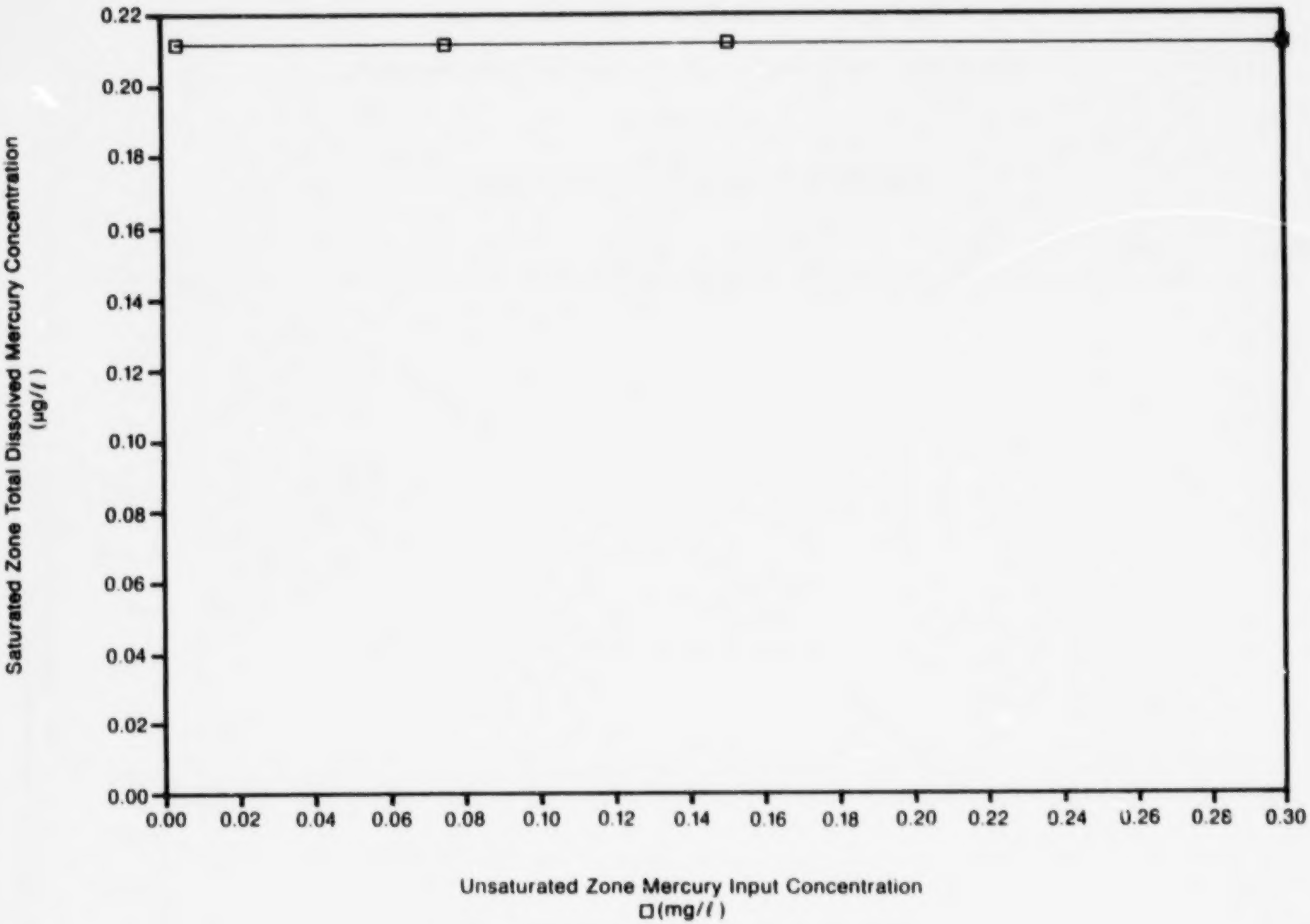


FIGURE B-3a

Saturated Zone Mercury Concentration after Speciation

Conditions: pH = 7.0, Redox = 500 mv

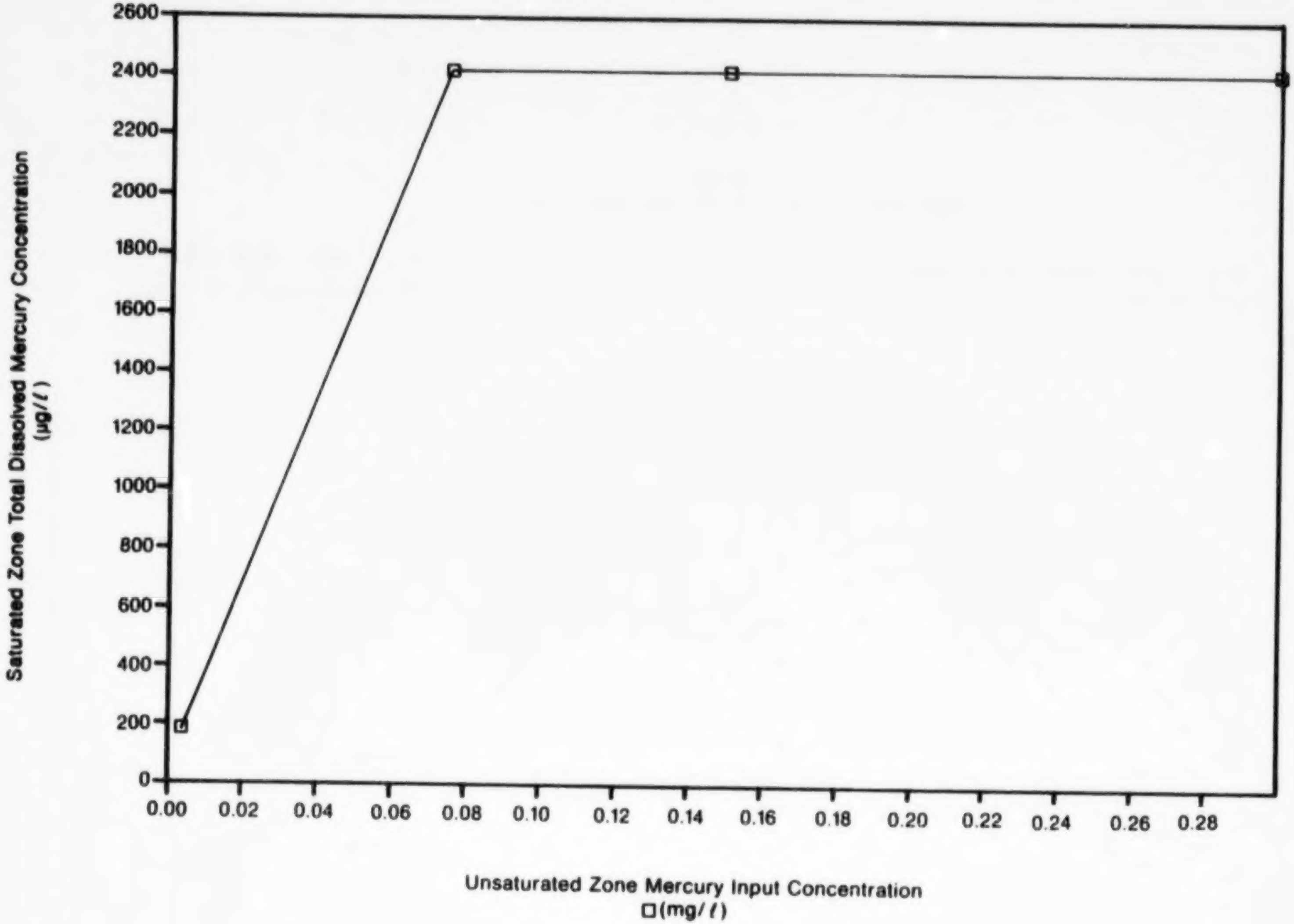


FIGURE B-3b

Saturated Zone Mercury Concentration after Speciation

Conditions: pH = 7.0, Redox = 150 mv

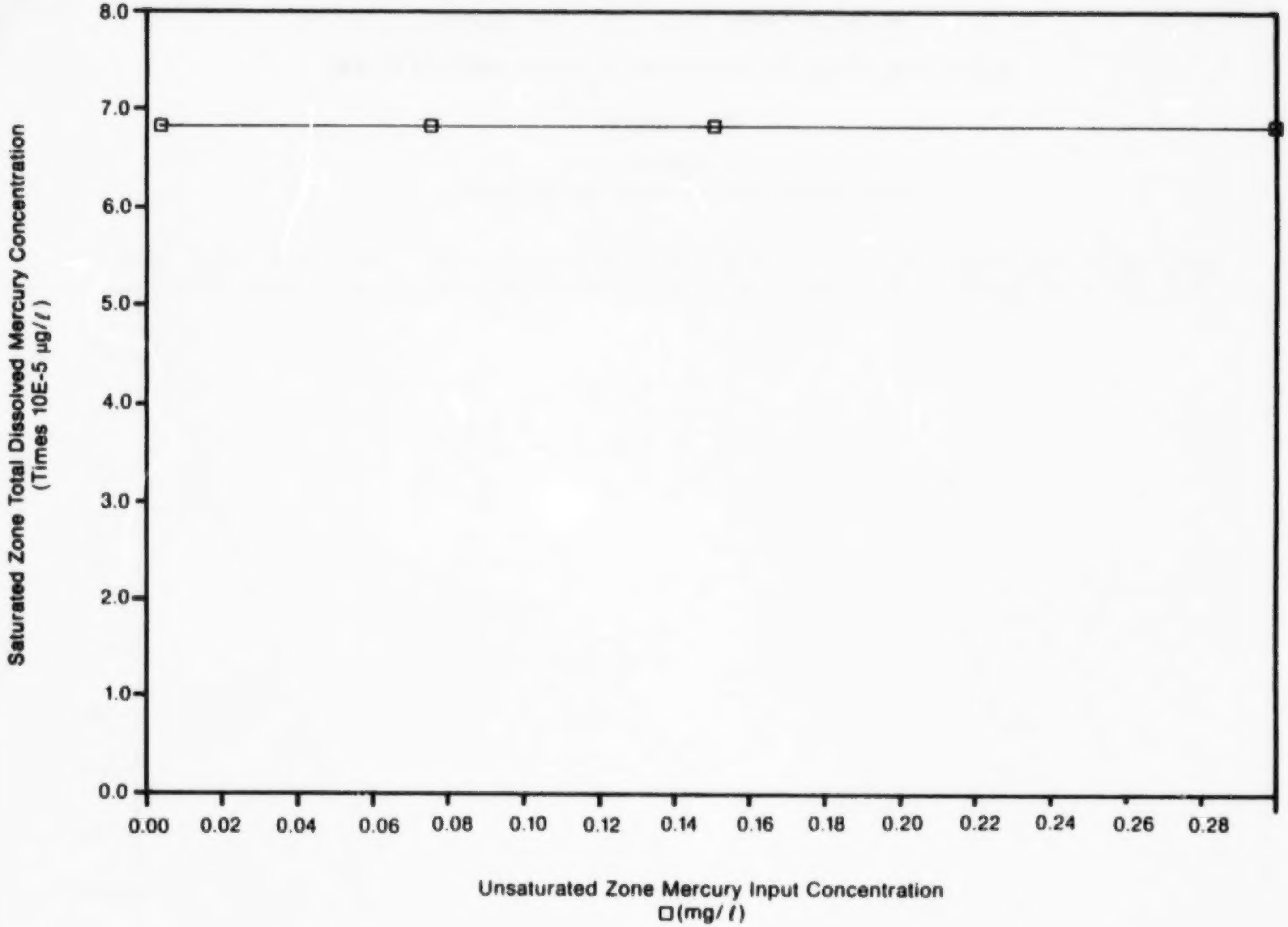


FIGURE B-3c

Saturated Zone Mercury Concentration after Speciation

Conditions: pH = 7.0, Redox = -200 mv

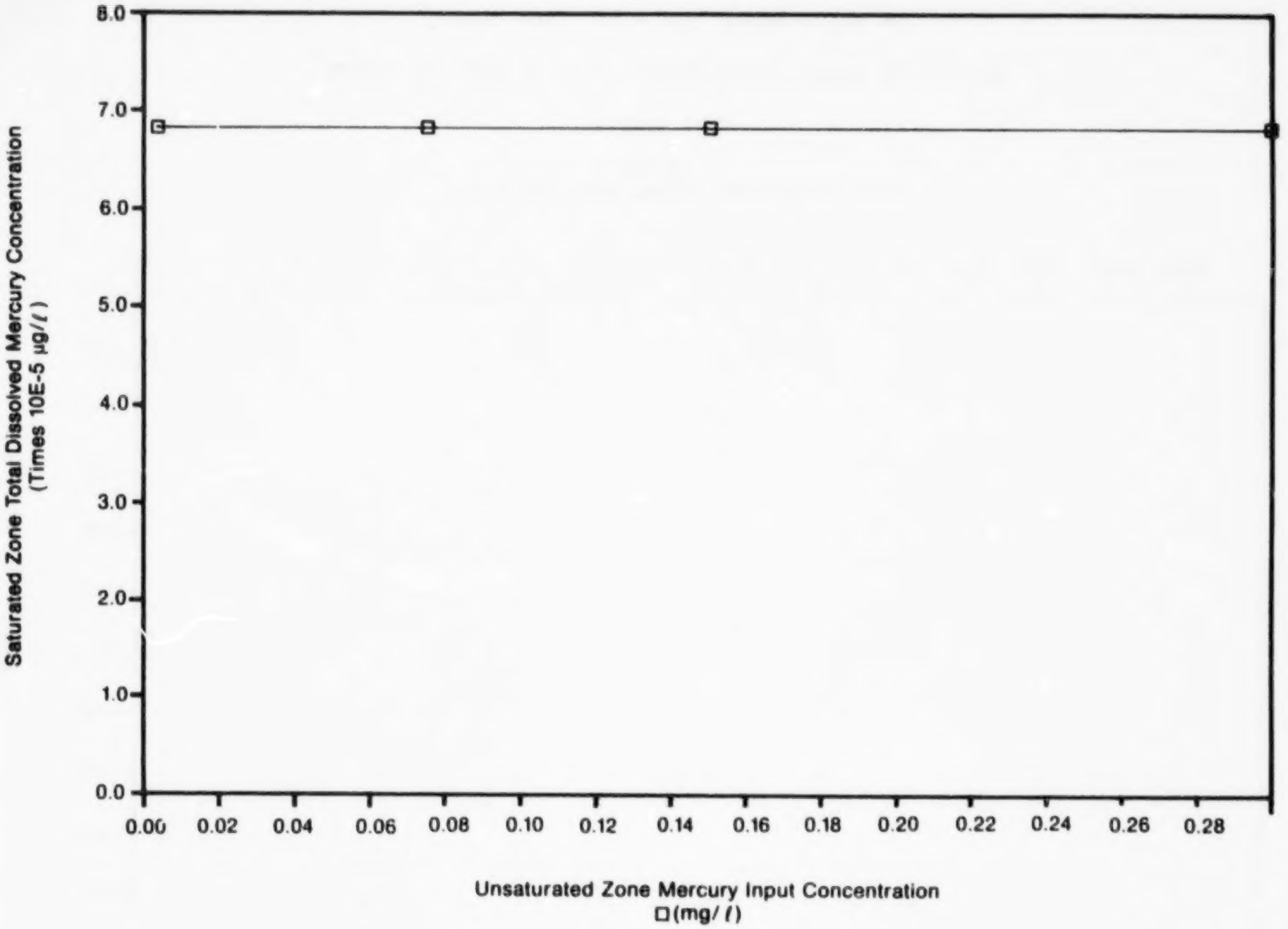


FIGURE B-3c

Saturated Zone Mercury Concentration after Speciation

Conditions: pH = 7.0, Redox = -200 mv

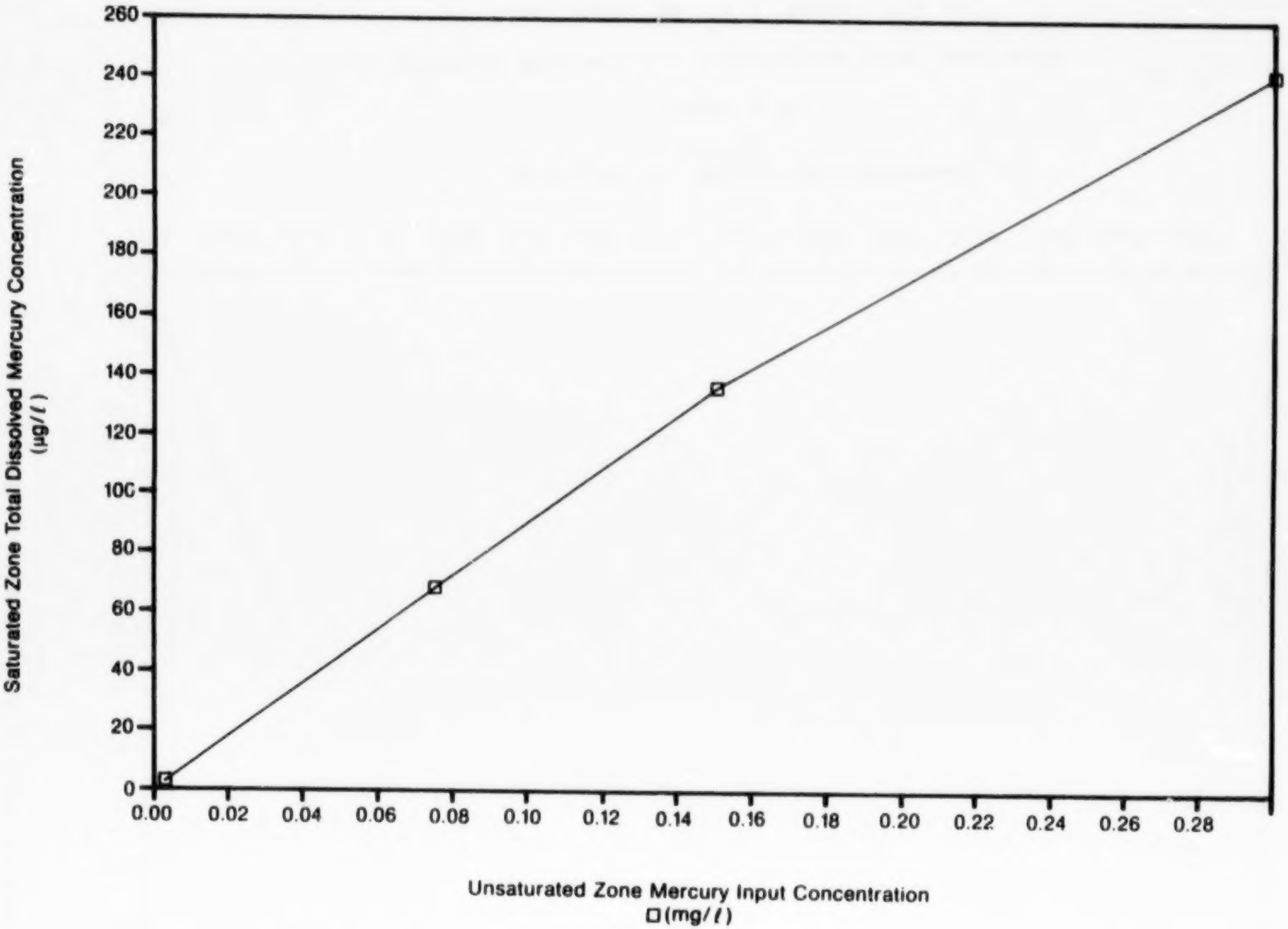


FIGURE B-3d

Saturated Zone Mercury Concentration after Speciation

Conditions: pH = 6.0, Redox = 500 mv

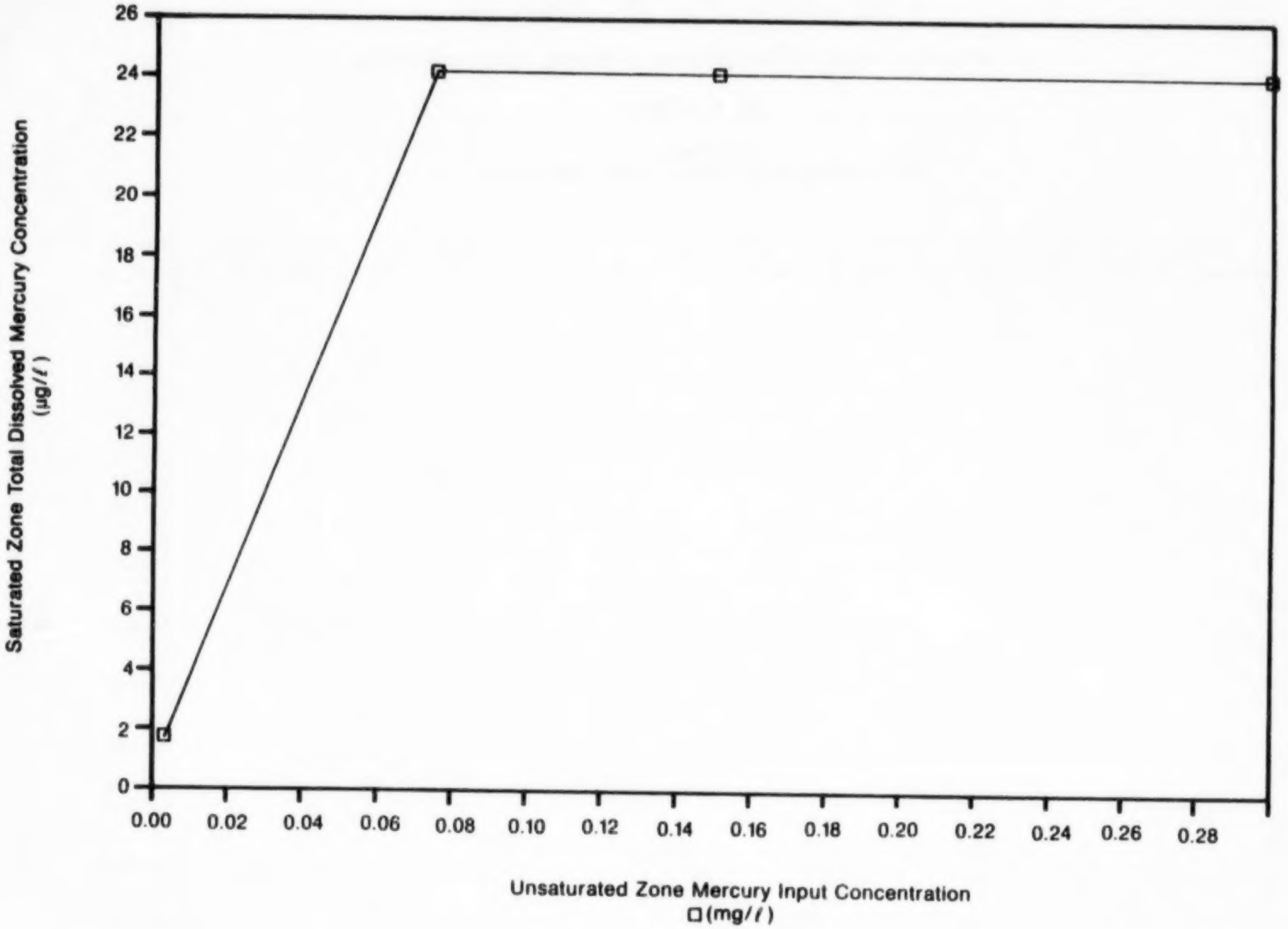


FIGURE B-3e

Saturated Zone Mercury Concentration after Speciation

Conditions: pH = 6.0, Redox = 150 mv

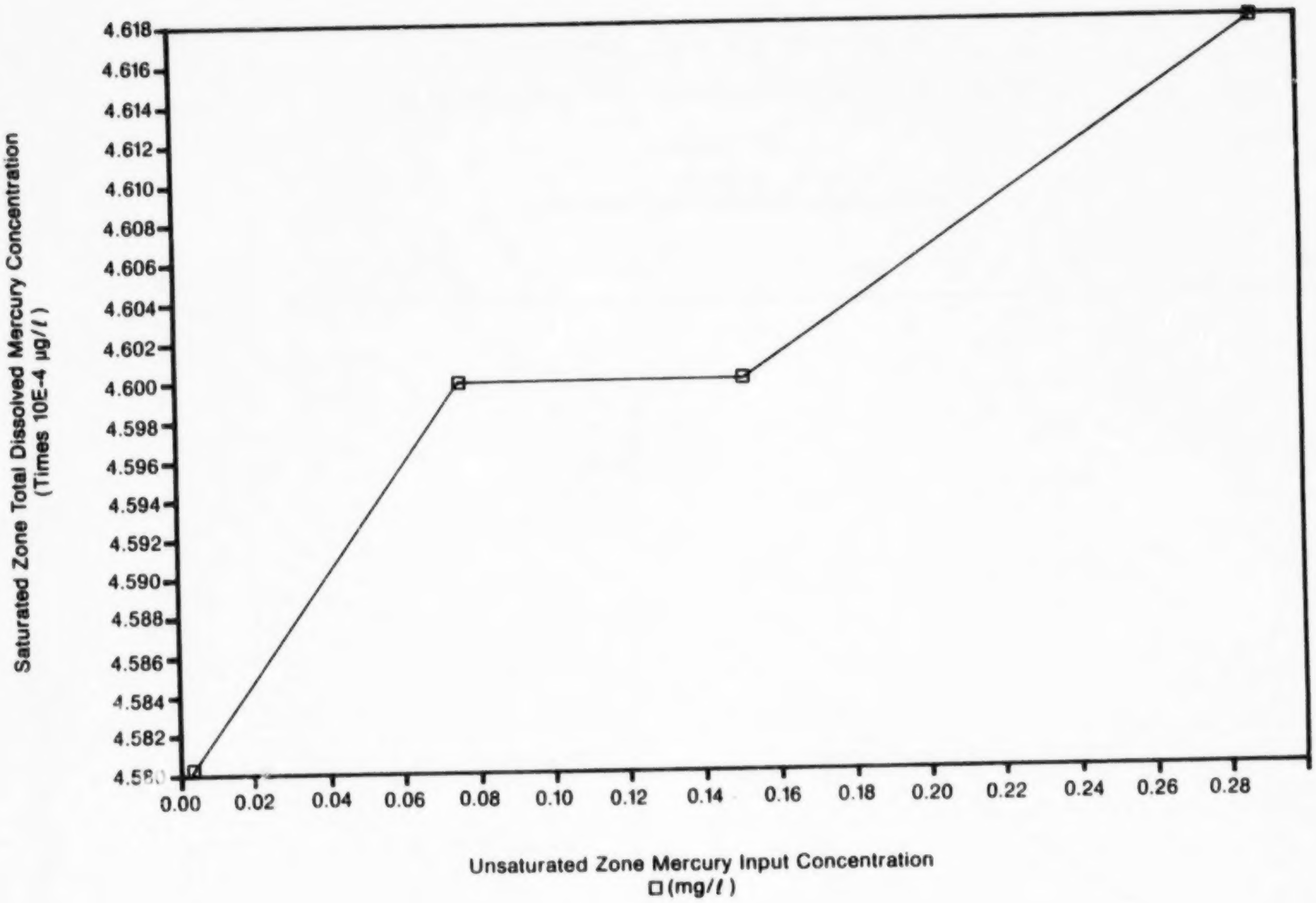


FIGURE B-3f

Saturated Zone Mercury Concentration after Speciation

Conditions: pH = 6.0, Redox = -200 mv

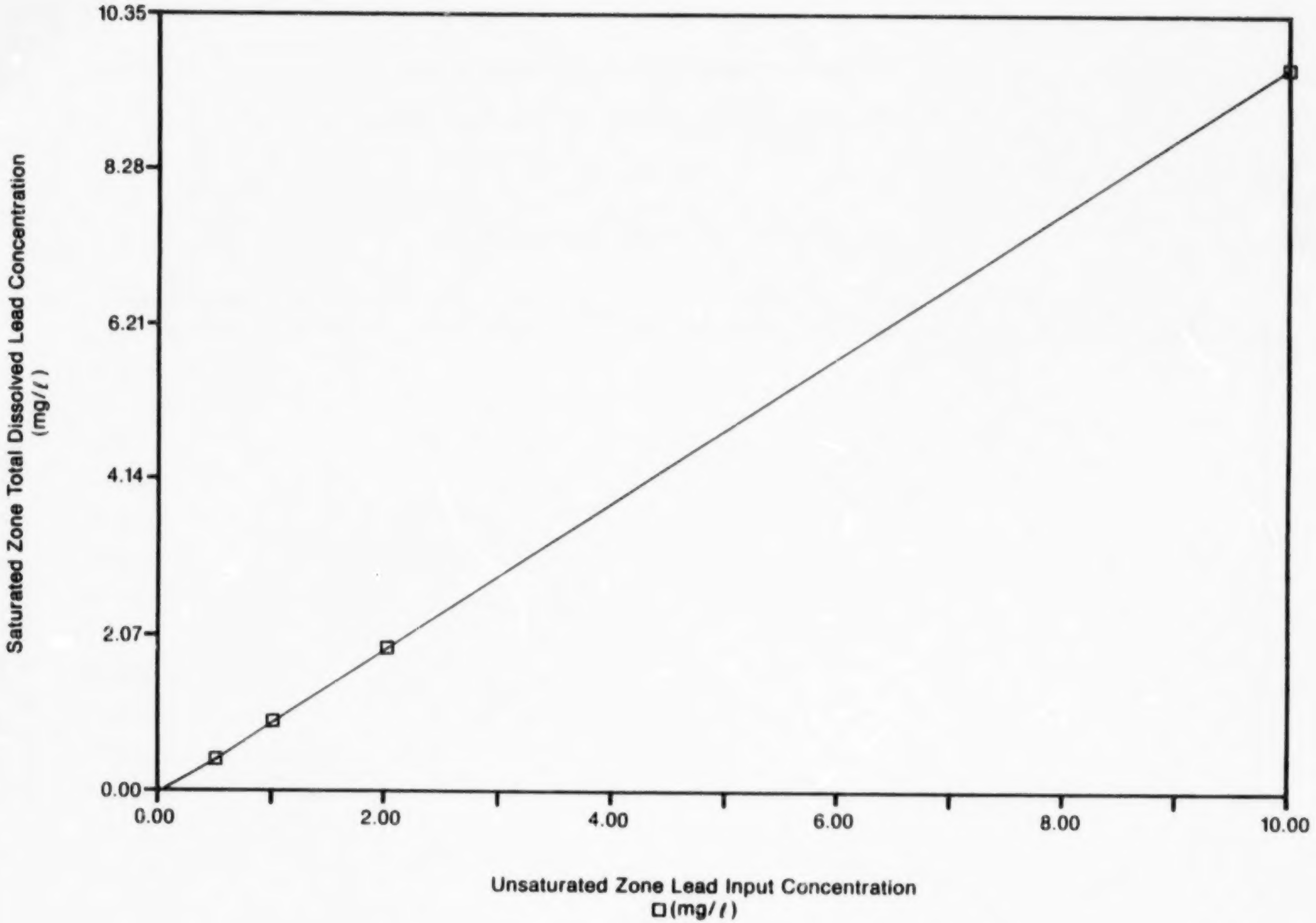


FIGURE B-4a

Saturated Zone Lead Concentration after Speciation

Conditions: pH = 7.0, Eh = 500 mv

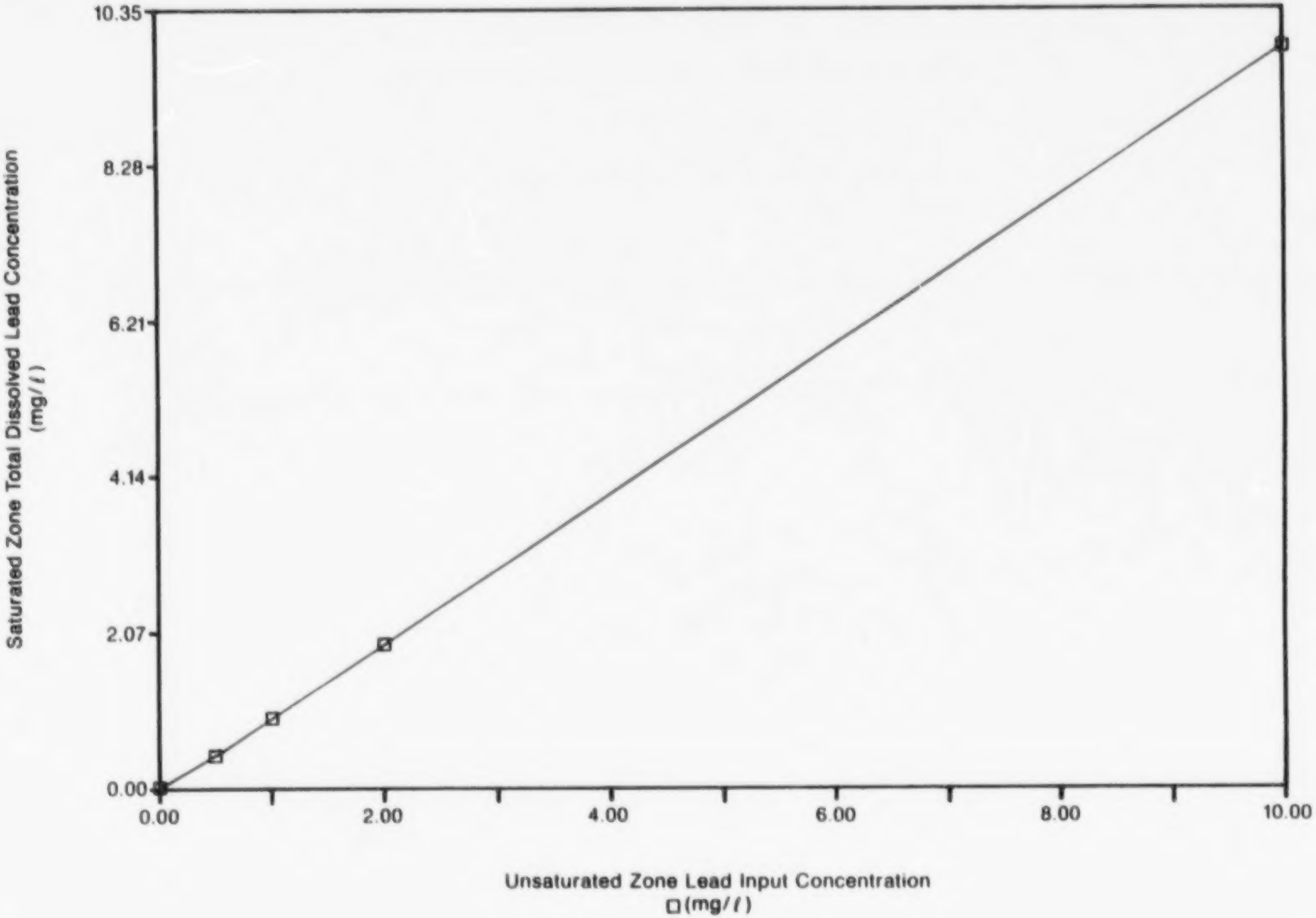


FIGURE B-4b

Saturated Zone Lead Concentration after Speciation

Conditions: pH = 7.0, Eh = 150 mv

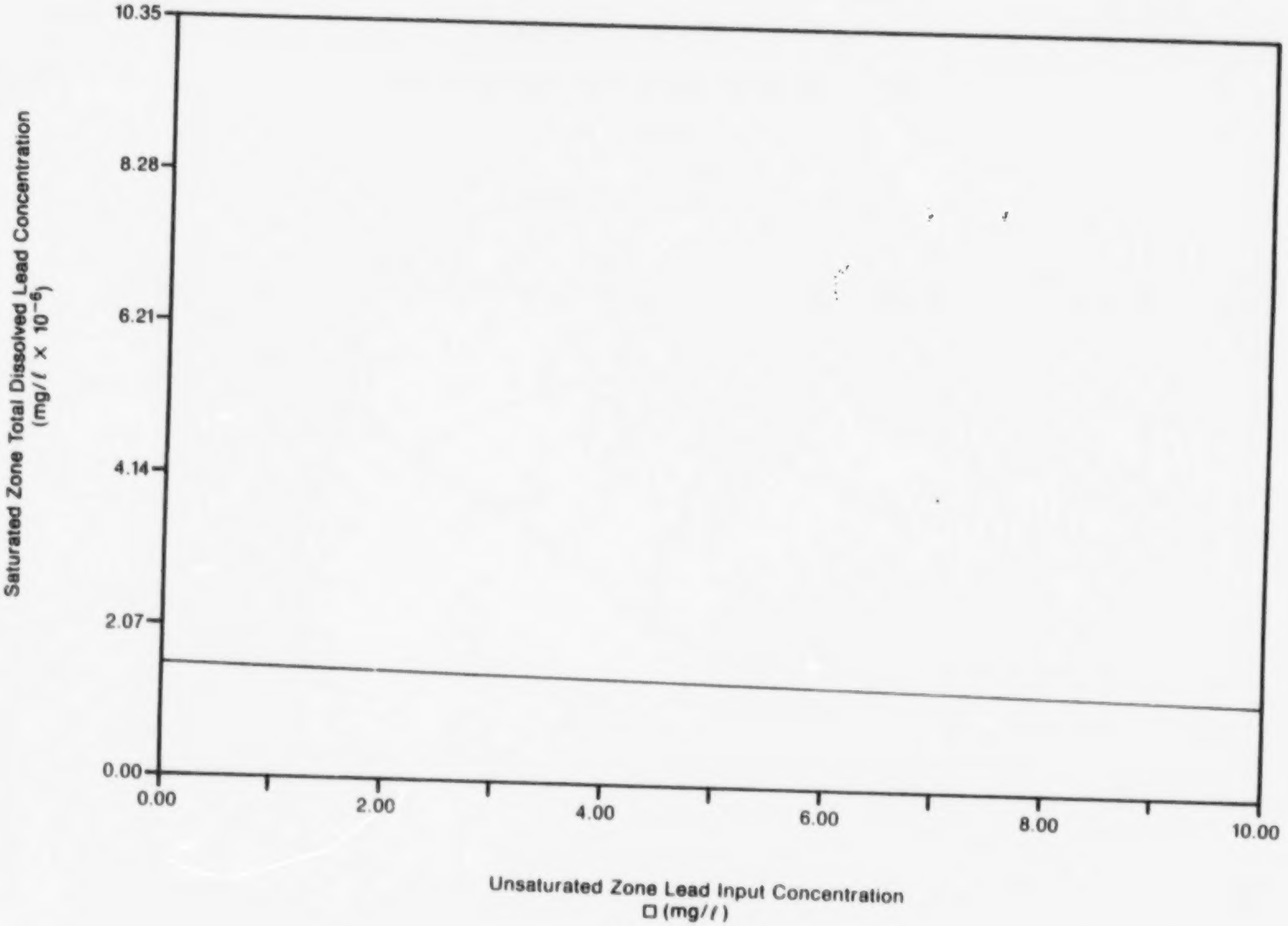


FIGURE B-4c

Saturated Zone Lead Concentration after Speciation

Conditions: pH = 6.0, Eh = -200 mv

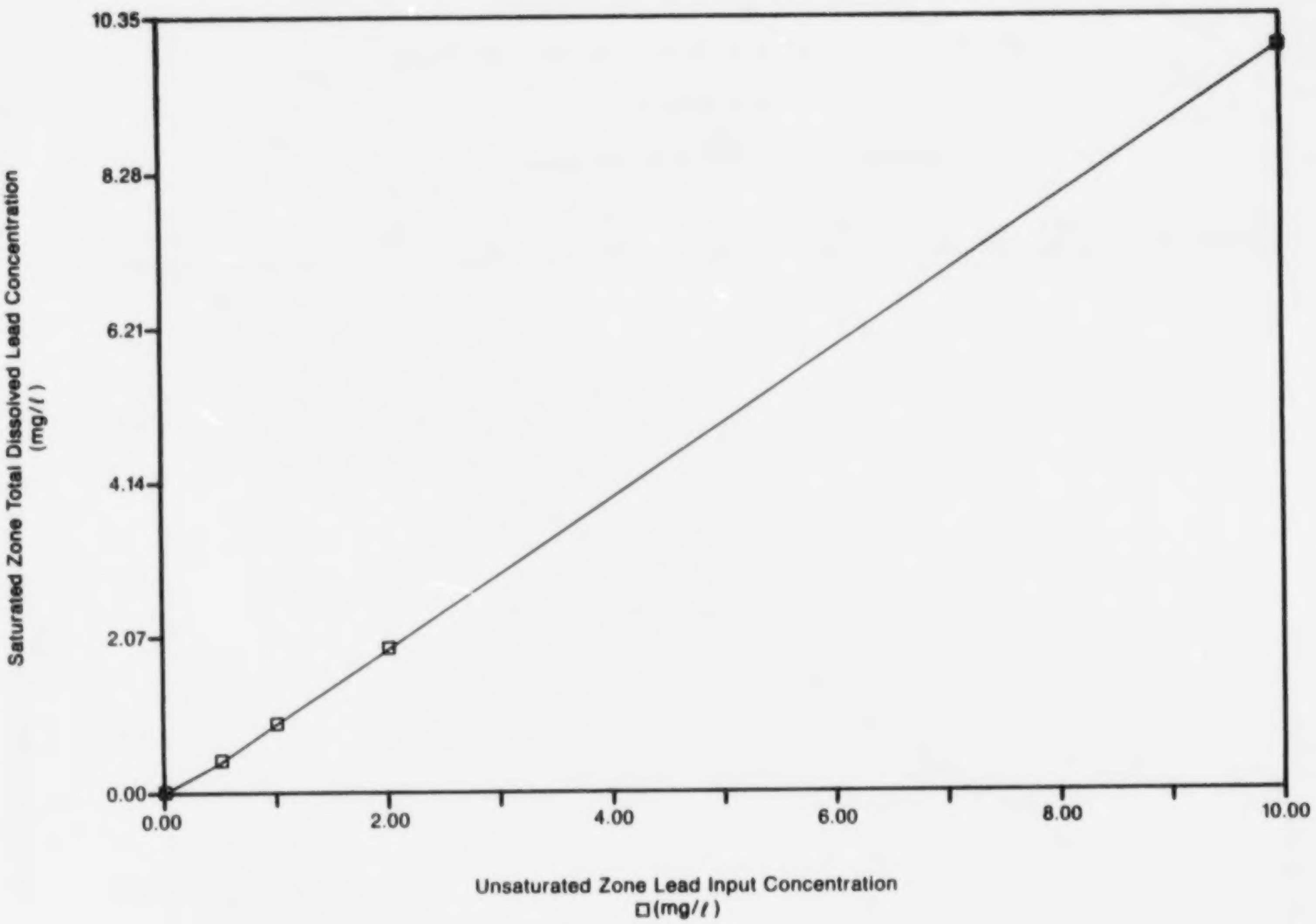


FIGURE B-4d

Saturated Zone Lead Concentration after Speciation

Conditions: pH = 6.0, Eh = 500 mv

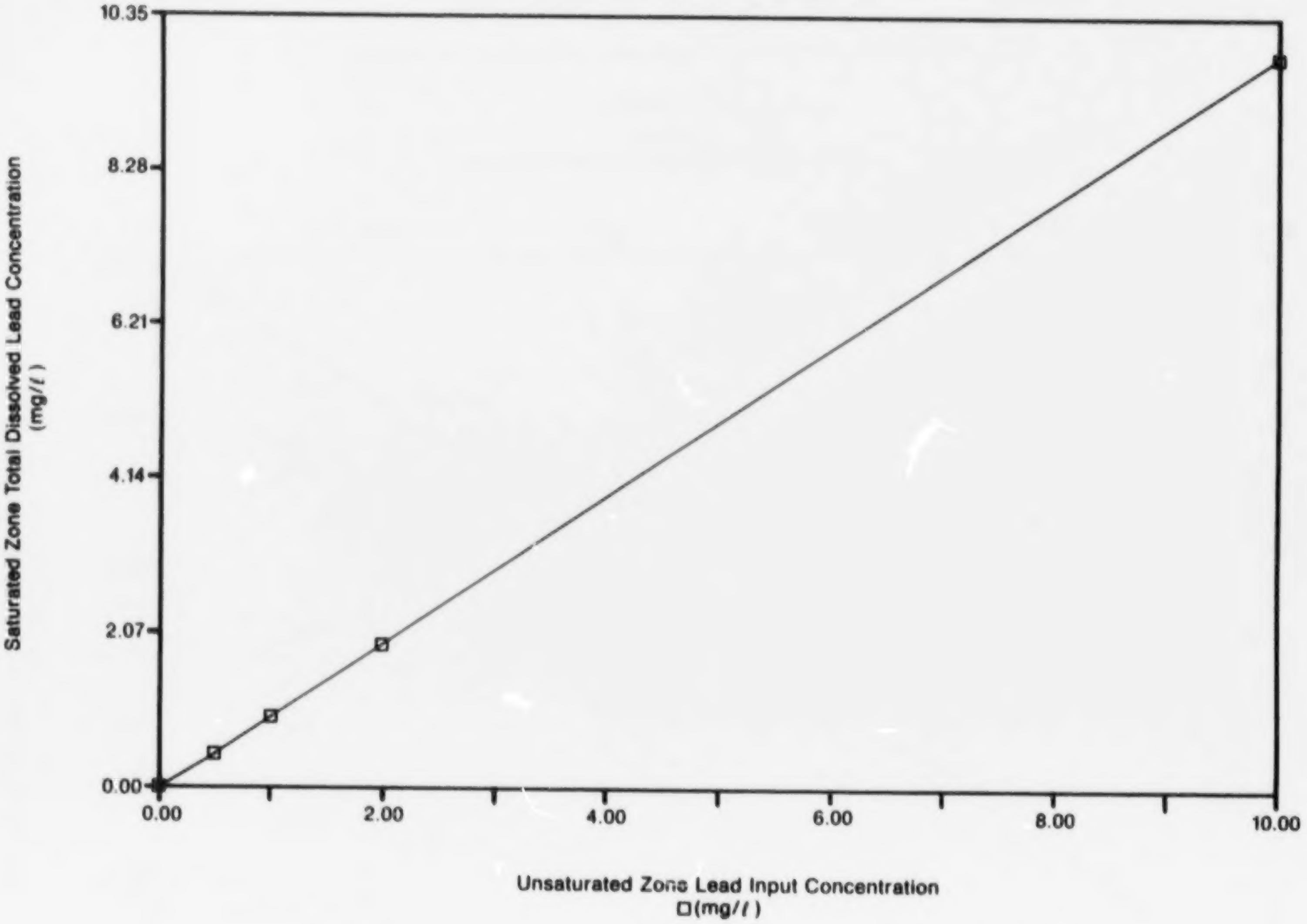


FIGURE B-4e

Saturated Zone Lead Concentration after Speciation

Conditions: pH = 6.0, Eh = 150 mv

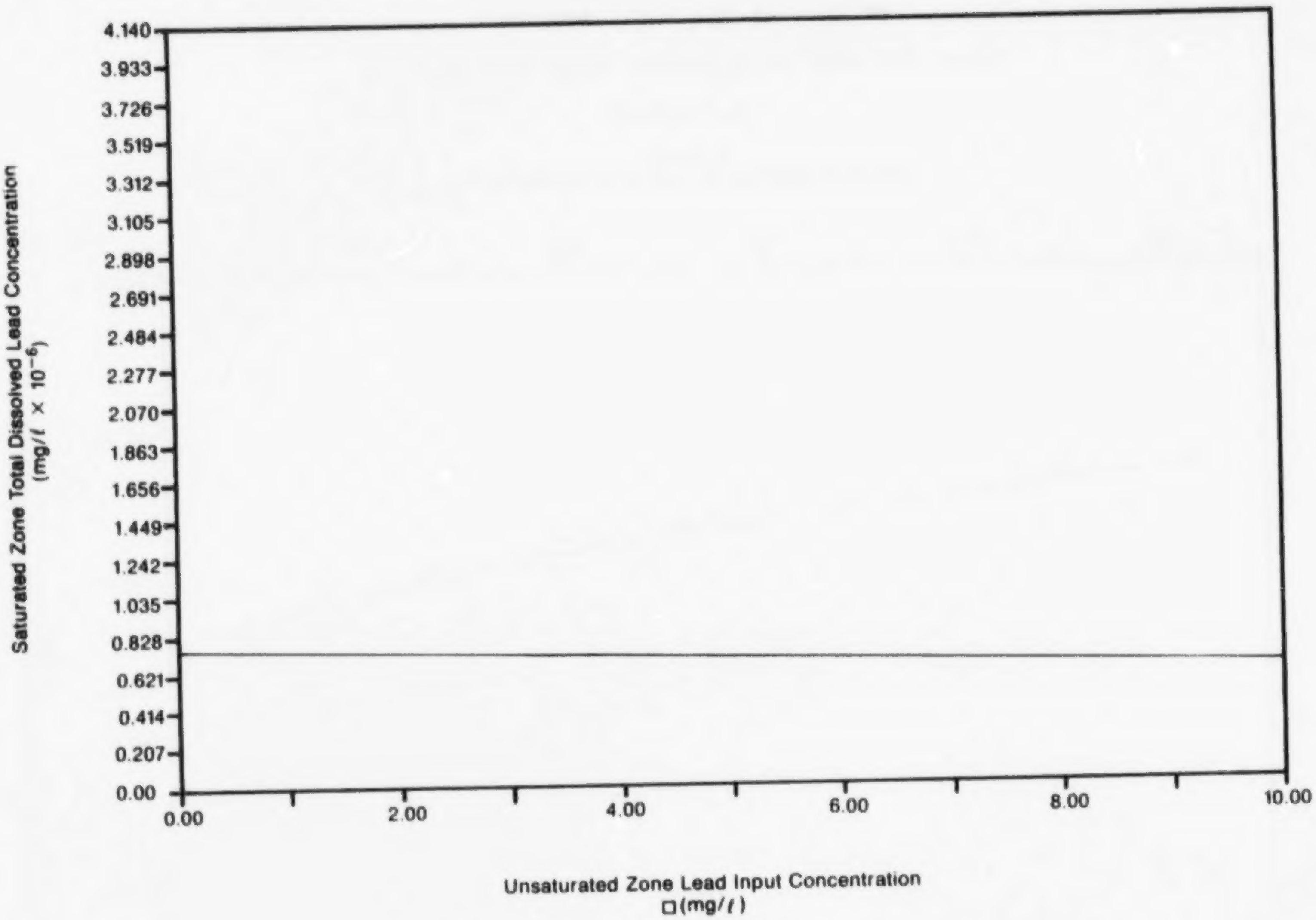


FIGURE B-4f

Saturated Zone Lead Concentration after Speciation

Conditions: pH = 7.0, Eh = -200 mv

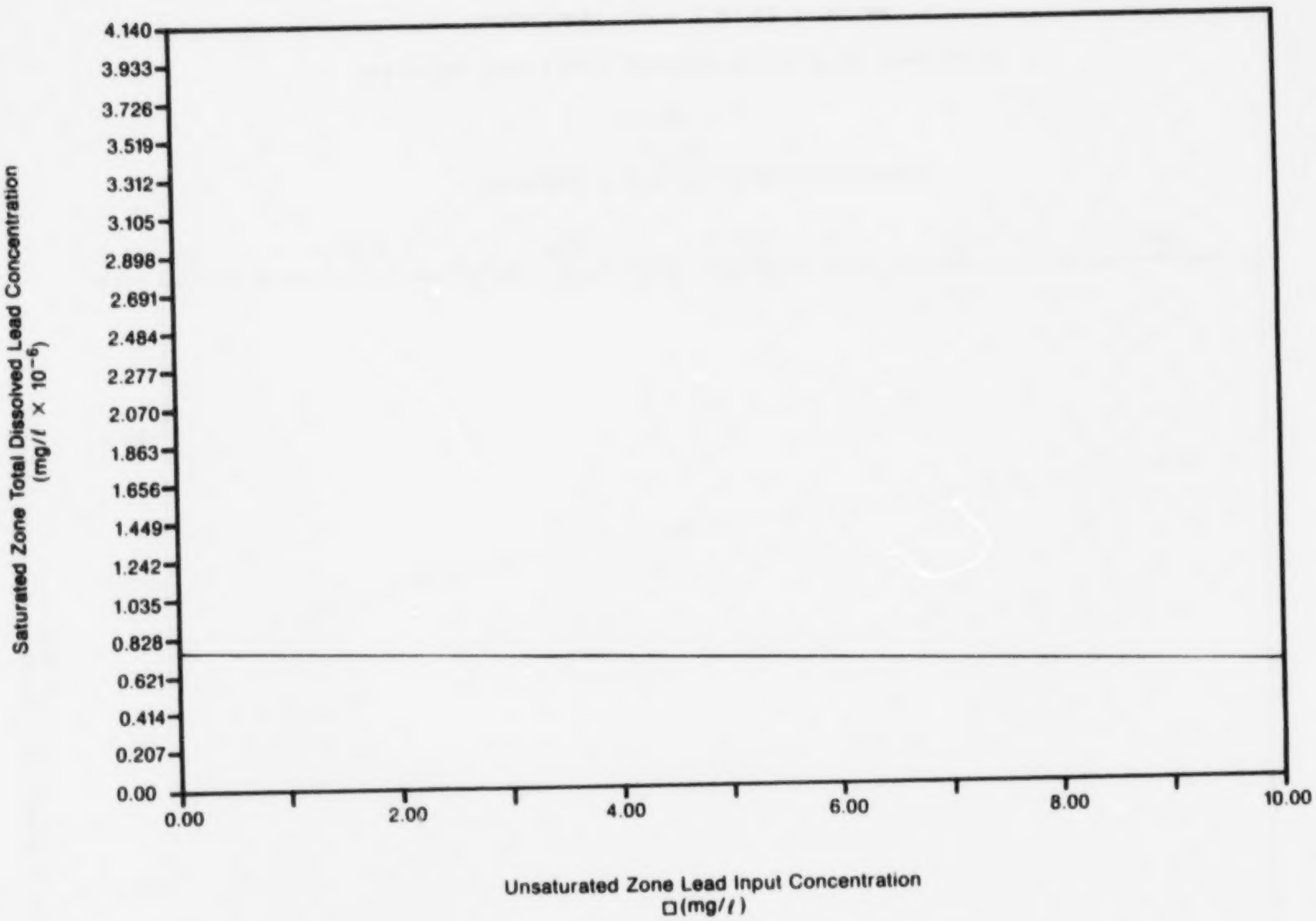


FIGURE B-4f

Saturated Zone Lead Concentration after Speciation

Conditions: pH = 7.0, Eh = -200 mv

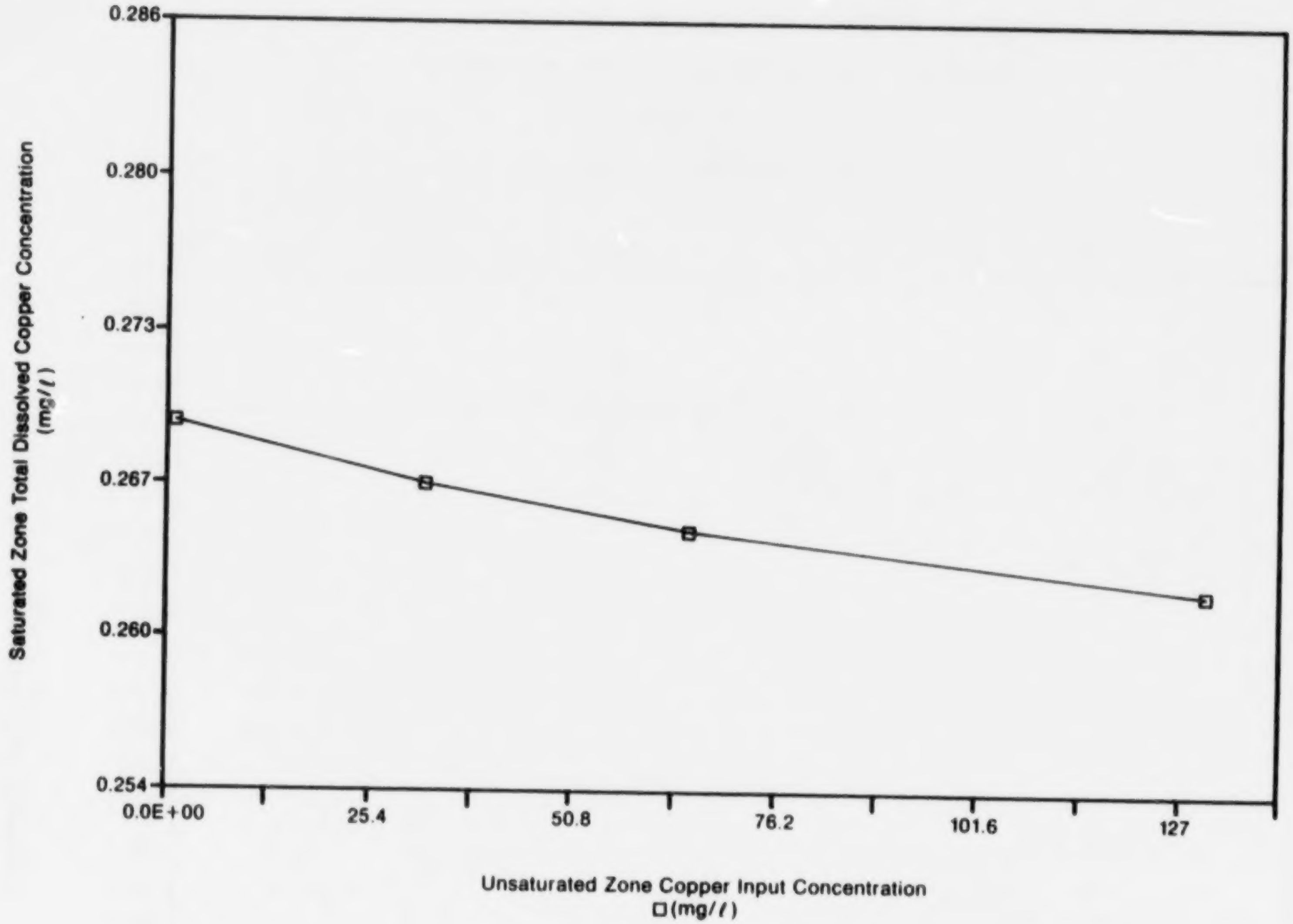


FIGURE B-5a

Saturated Zone Copper Concentration after Speciation

Conditions: pH = 7.0, Eh = 500 mv

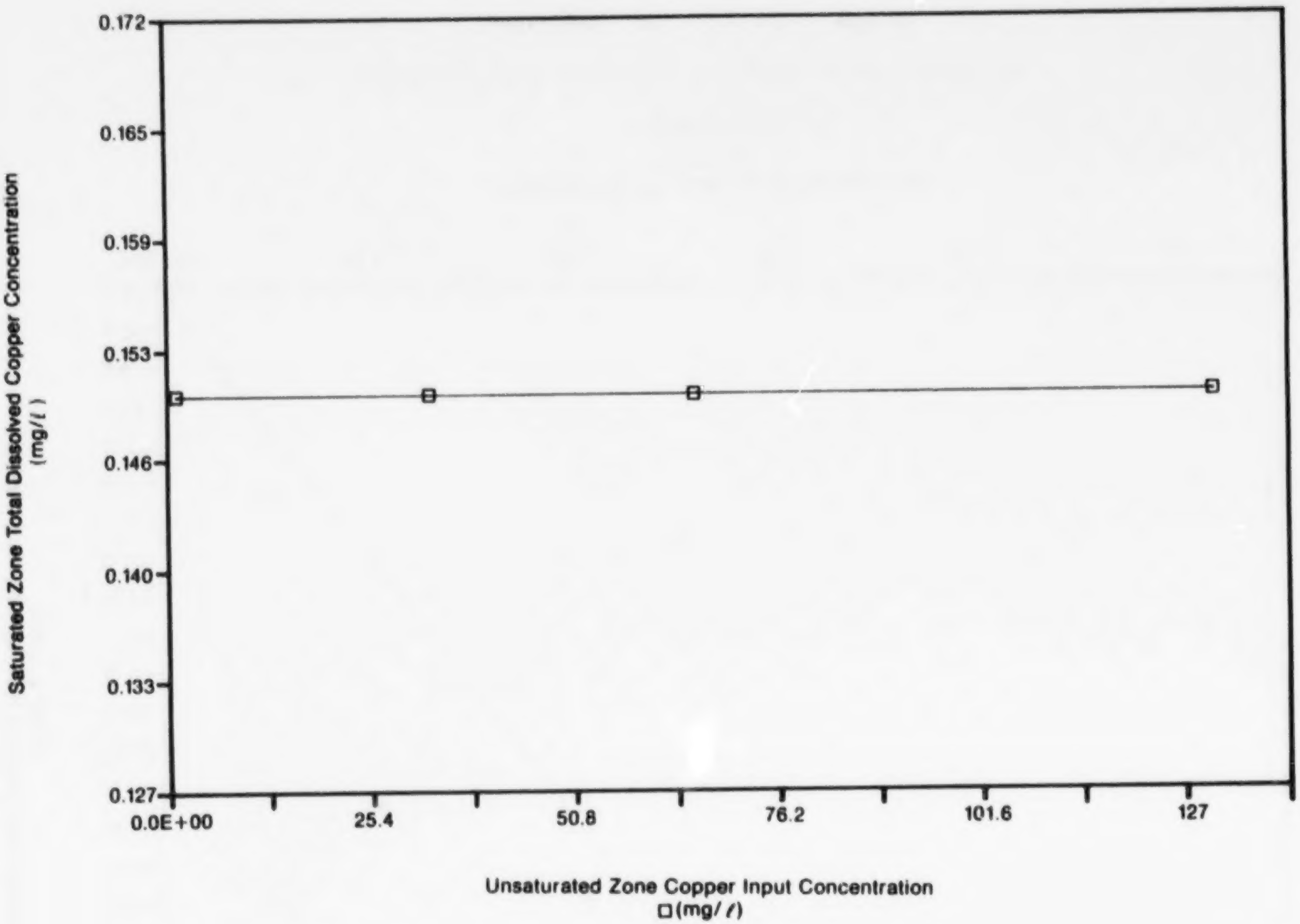


FIGURE B-5b

Saturated Zone Copper Concentration after Speciation

Conditions: pH = 7.0, Eh = 150 mv

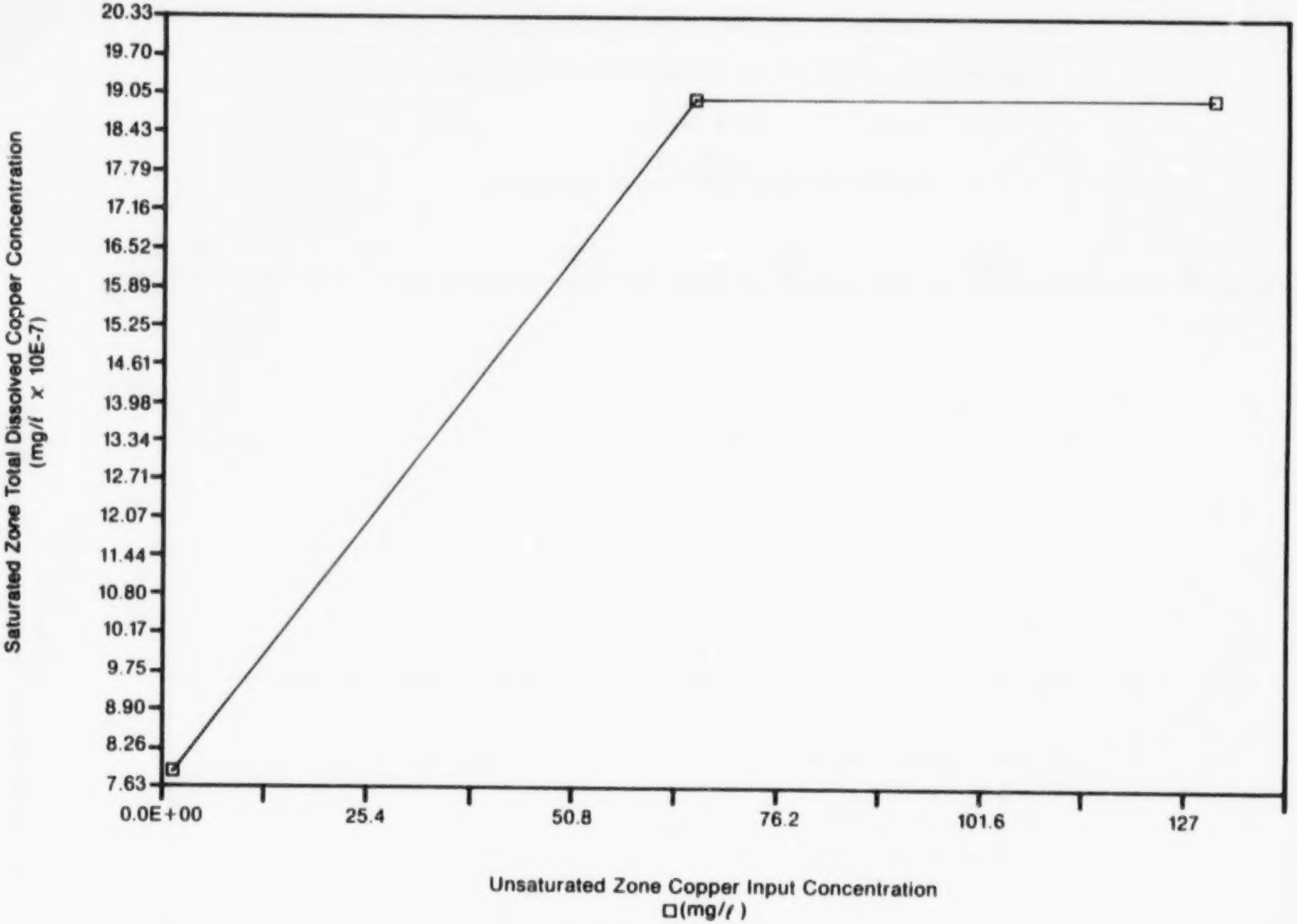


FIGURE B-5c

Saturated Zone Copper Concentration after Speciation

Conditions: pH = 7.0, Eh = -200 mv

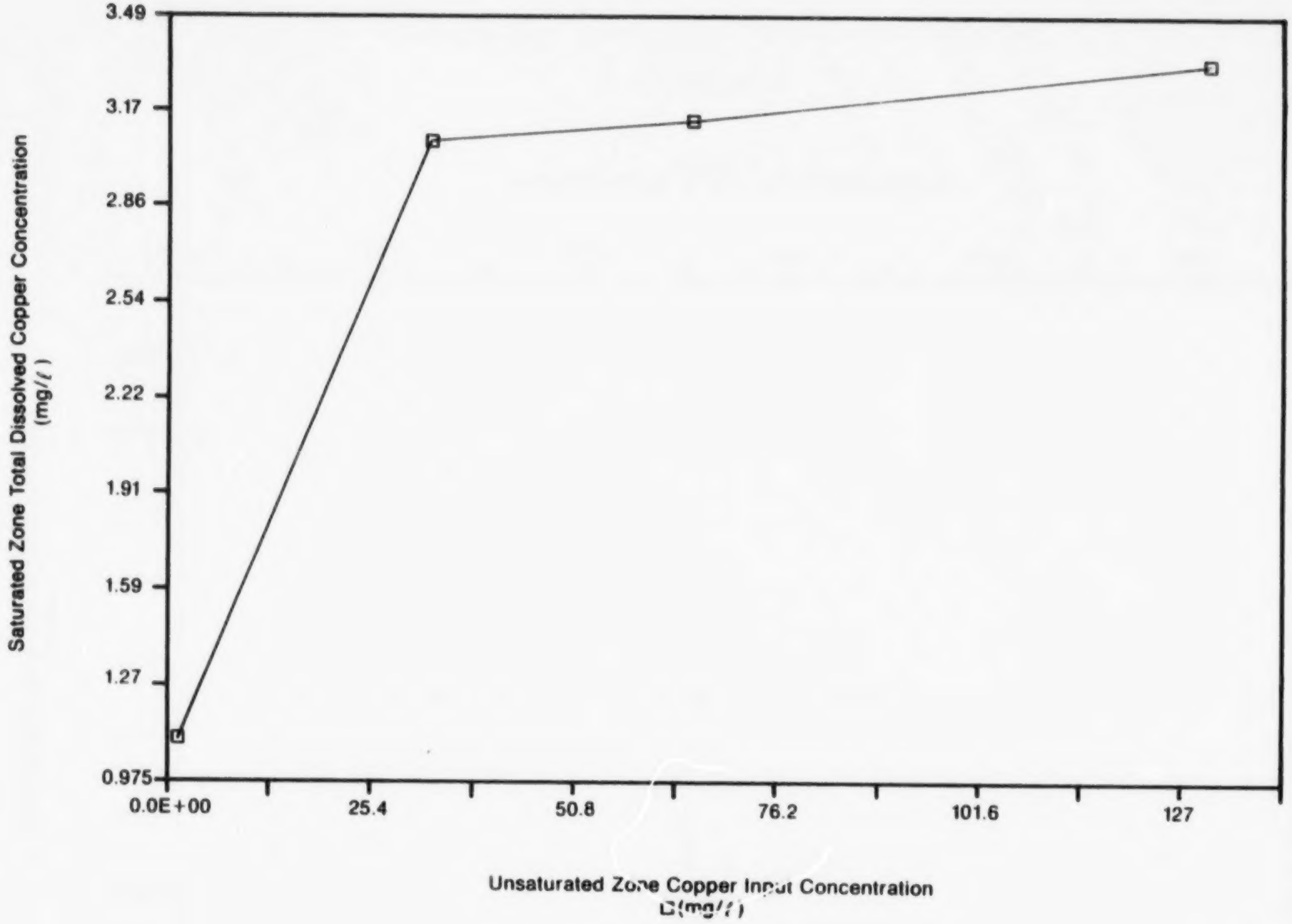


FIGURE B-5d

Saturated Zone Copper Concentration after Speciation

Conditions: pH = 6.0, Eh = 500 mv

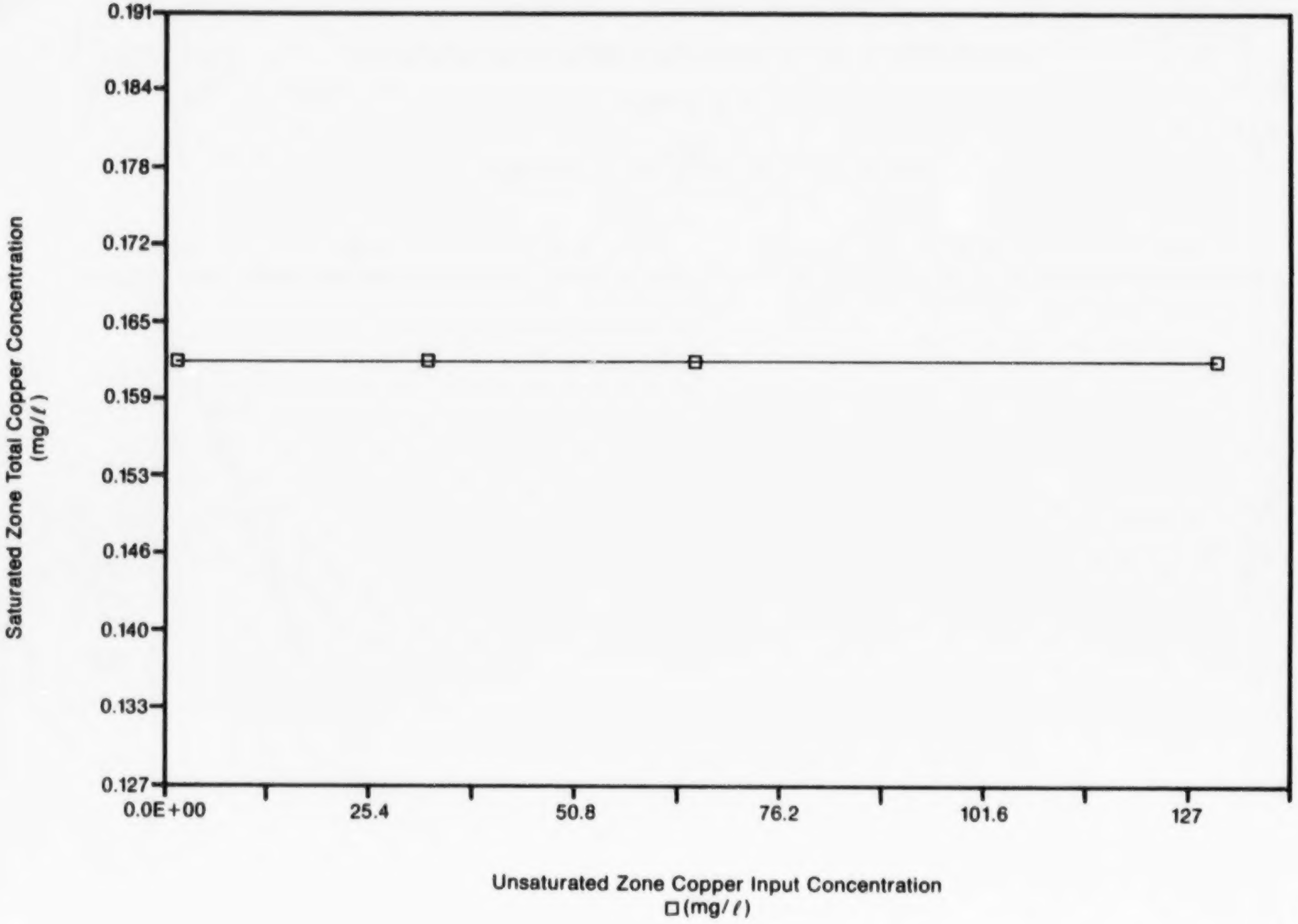


FIGURE B-5e

Saturated Zone Copper Concentration after Speciation

Conditions: pH = 6.0, Eh = 150 mv

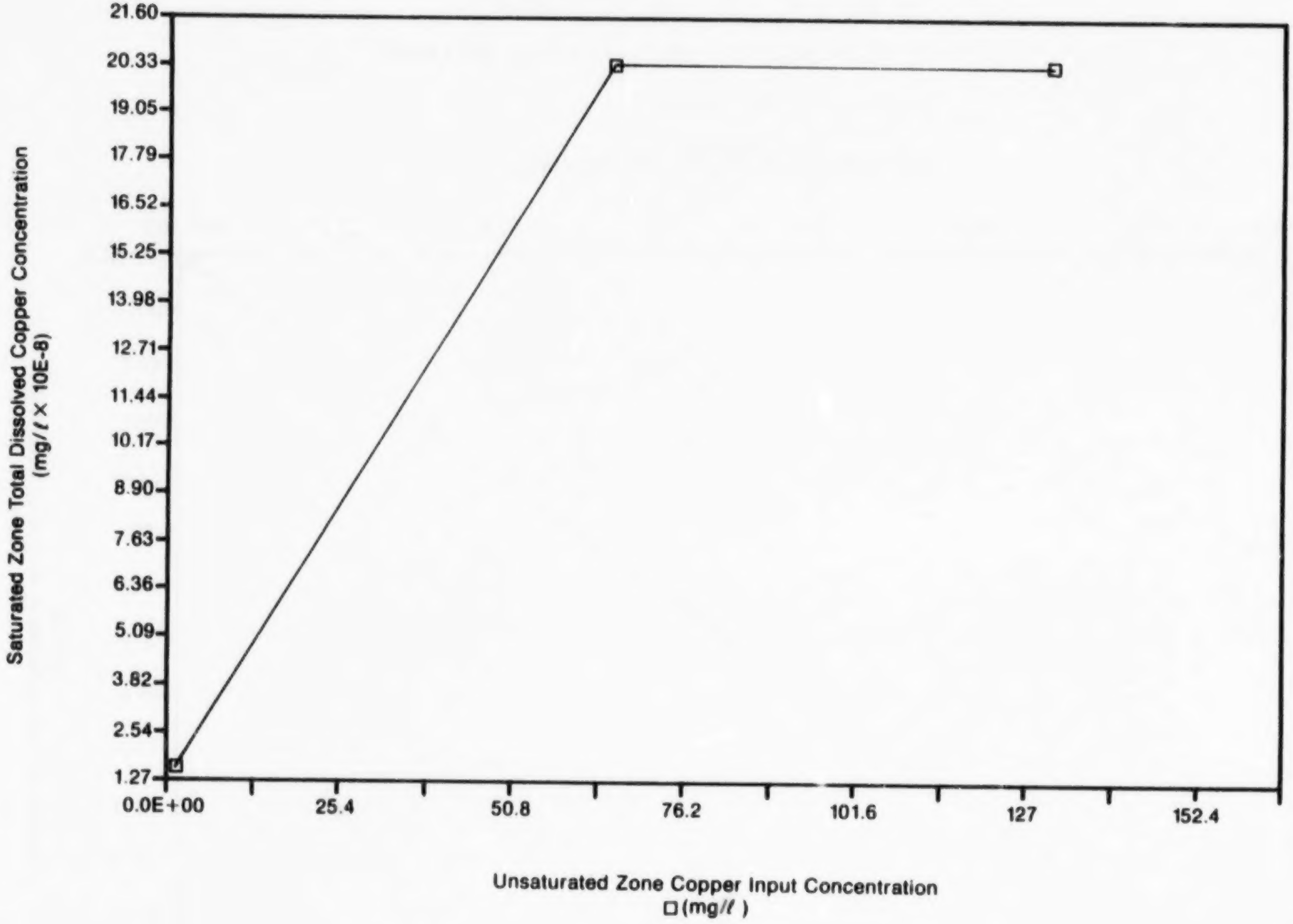


FIGURE B-5f

Saturated Zone Copper Concentration after Speciation

Conditions: pH = 6.0, Eh = -200 mv

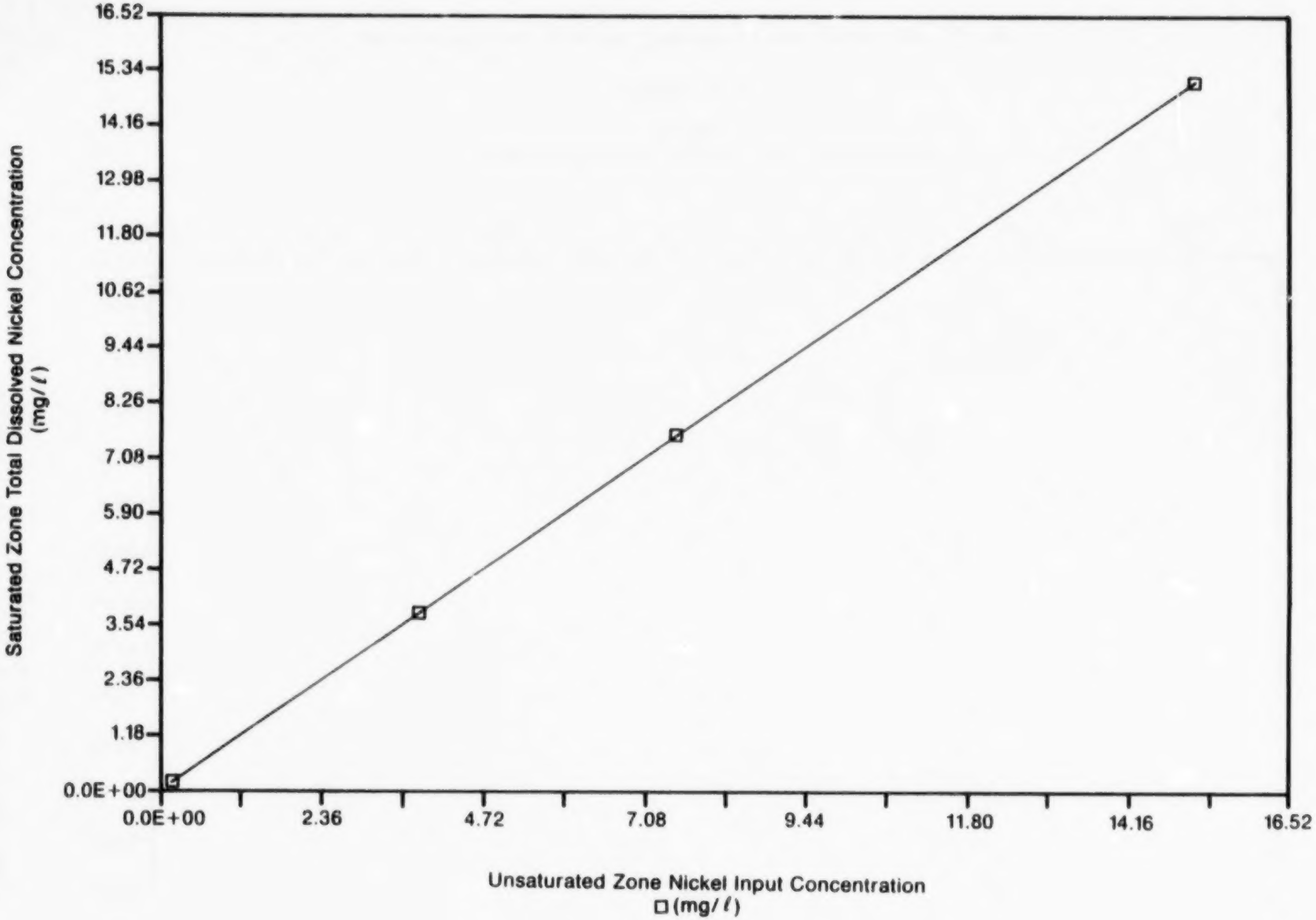


FIGURE B-6a

Saturated Zone Nickel Concentration after Speciation

Conditions: pH = 6.0, Eh = 500 mv

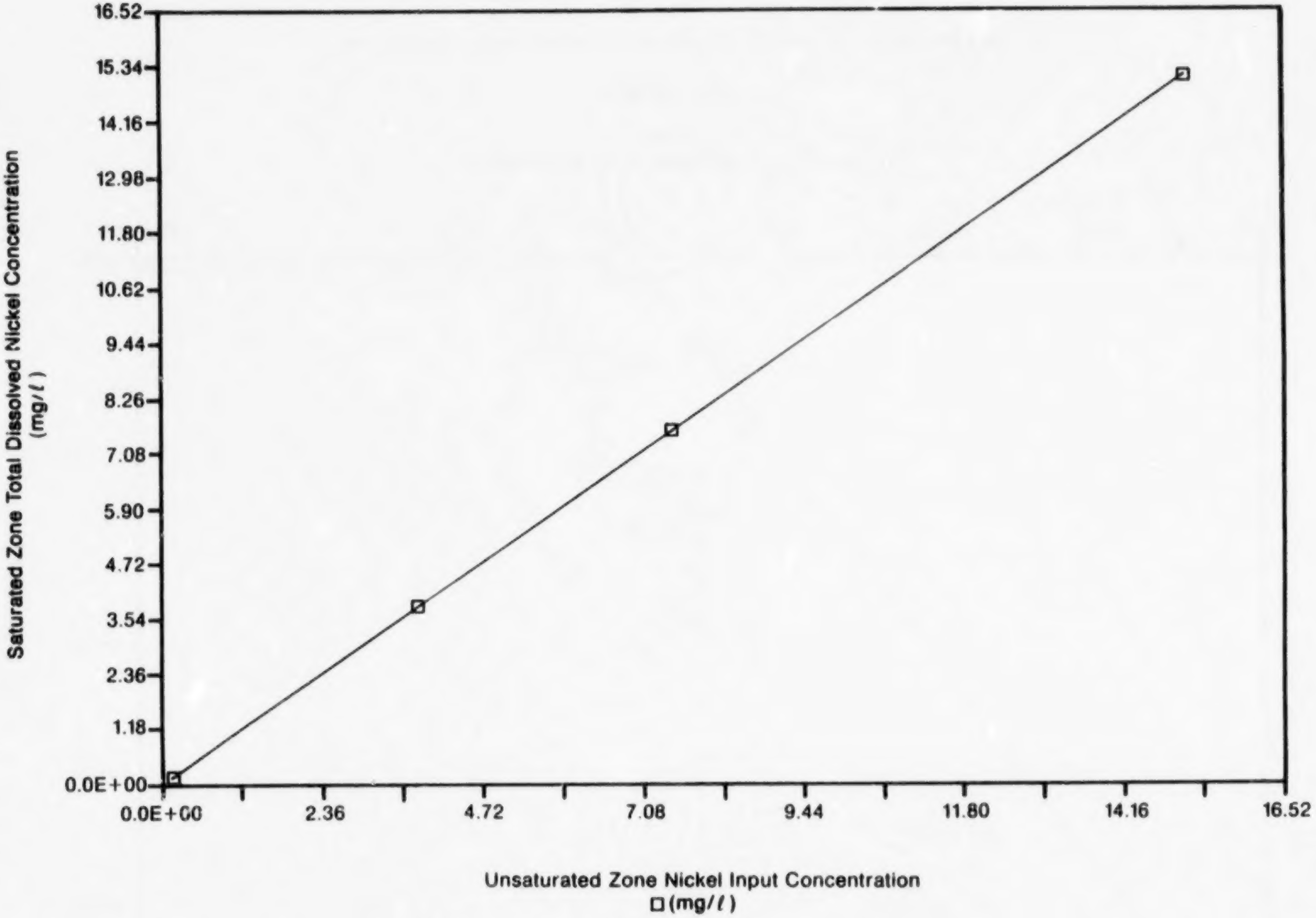


FIGURE B-6b

Saturated Zone Nickel Concentration after Speciation

Conditions: pH = 6.0, Eh = 150 mv

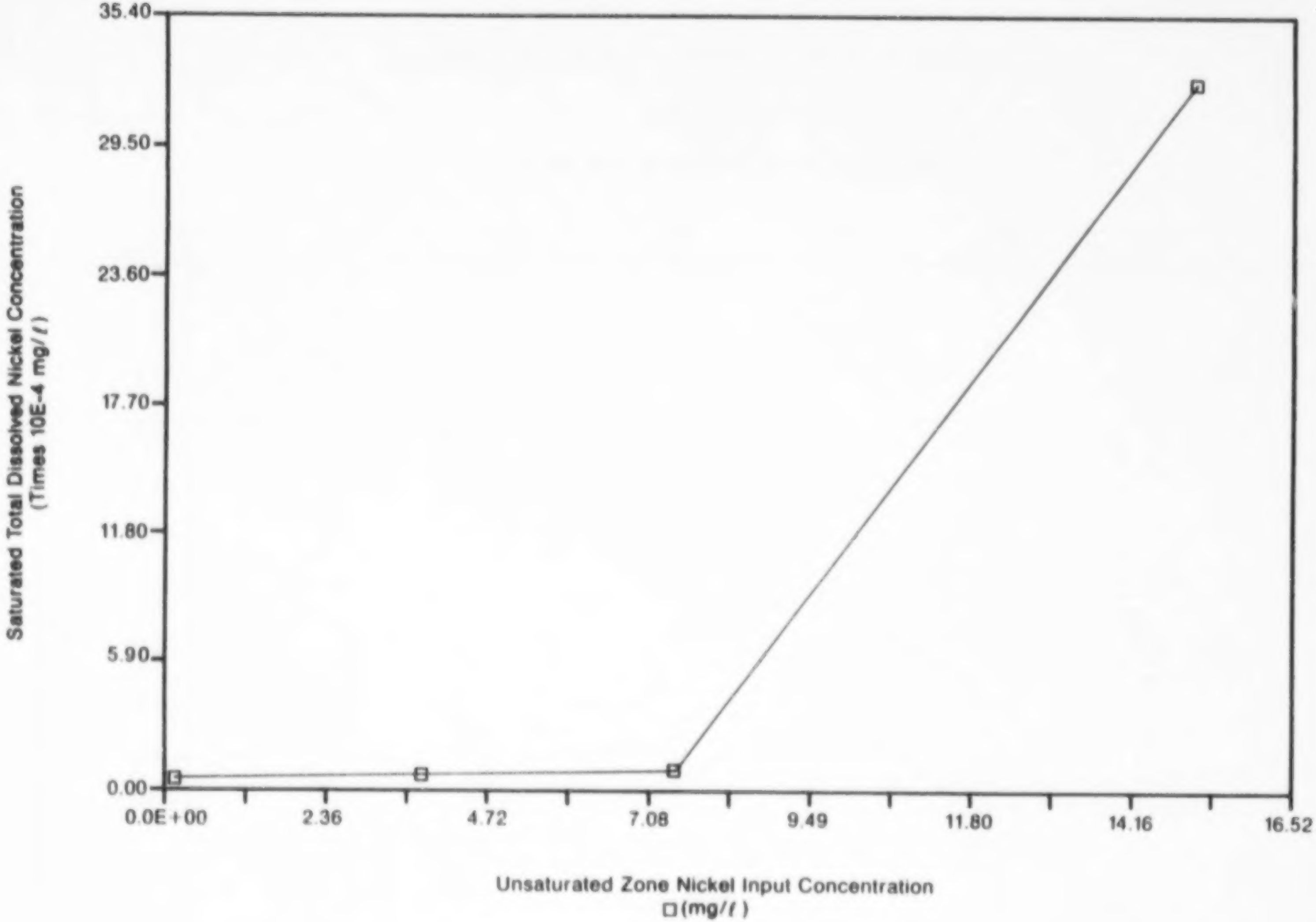


FIGURE B-6c

Saturated Zone Nickel Concentration after Speciation

Conditions: pH = 6.0, Eh = -200 mv

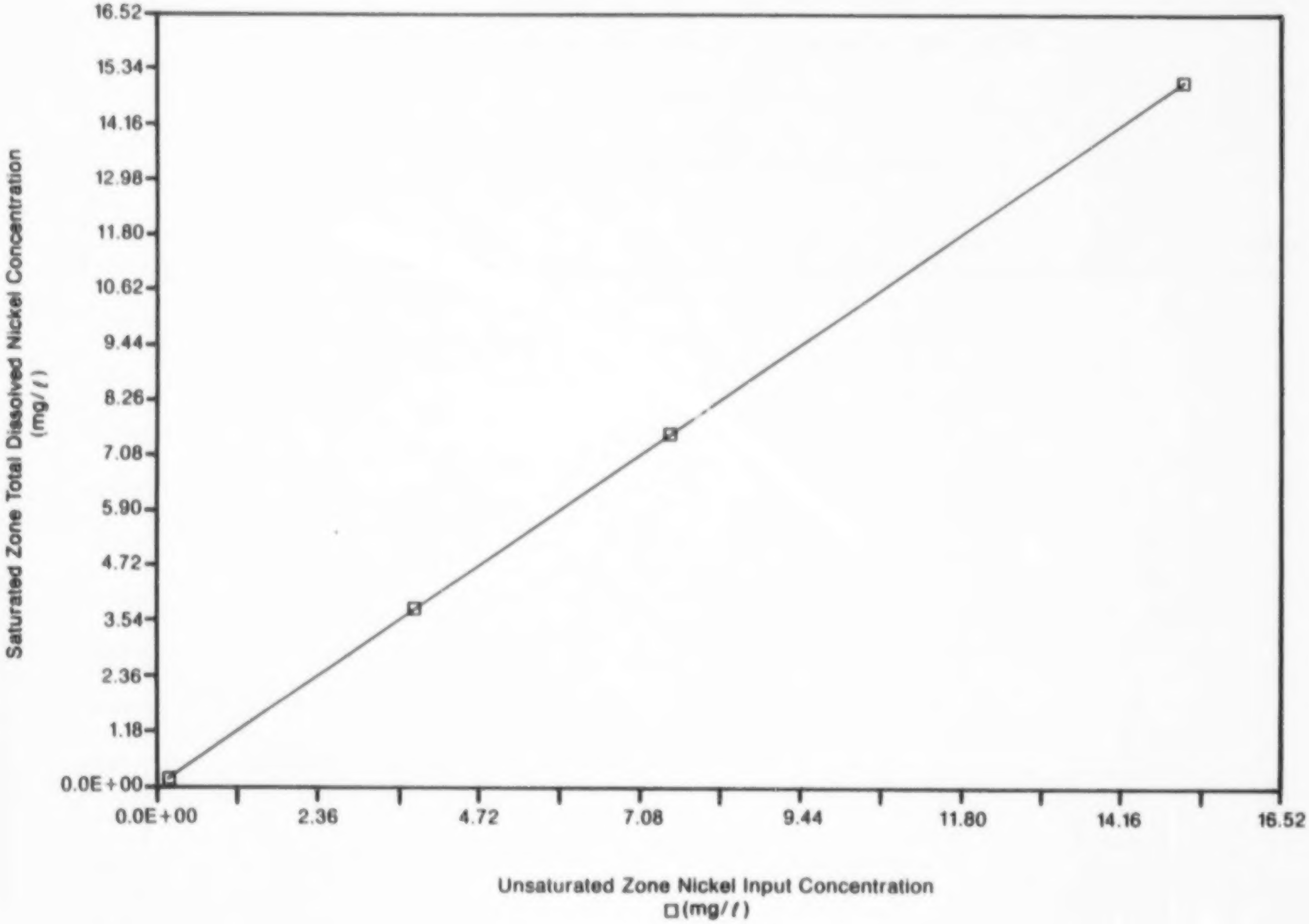


FIGURE B-6d

Saturated Zone Nickel Concentration after Speciation

Conditions: pH = 7.0, Eh = 500 mv

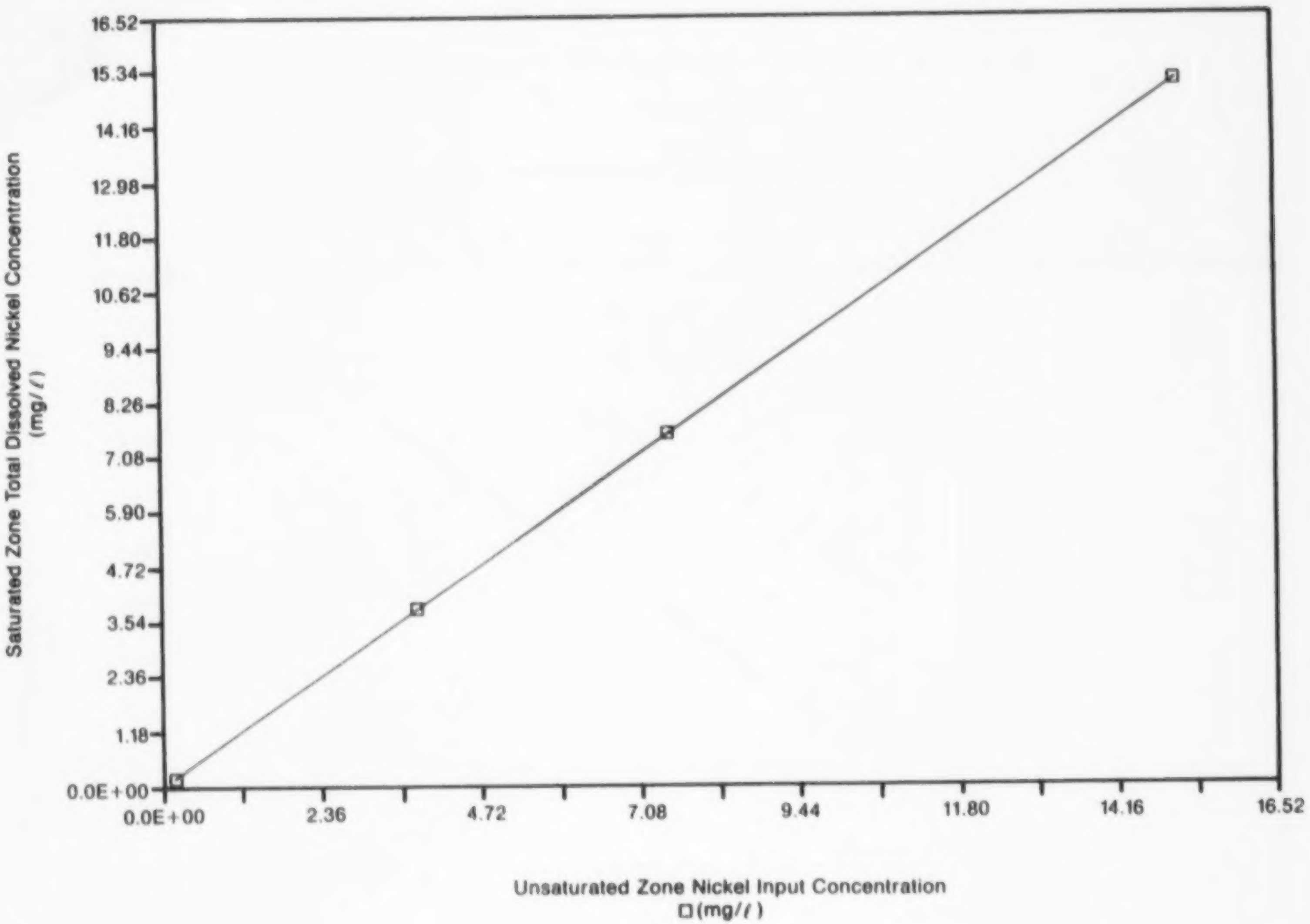


FIGURE B-6e

Saturated Zone Nickel Concentration after Speciation

Conditions: pH = 7.0, Eh = 150 mv

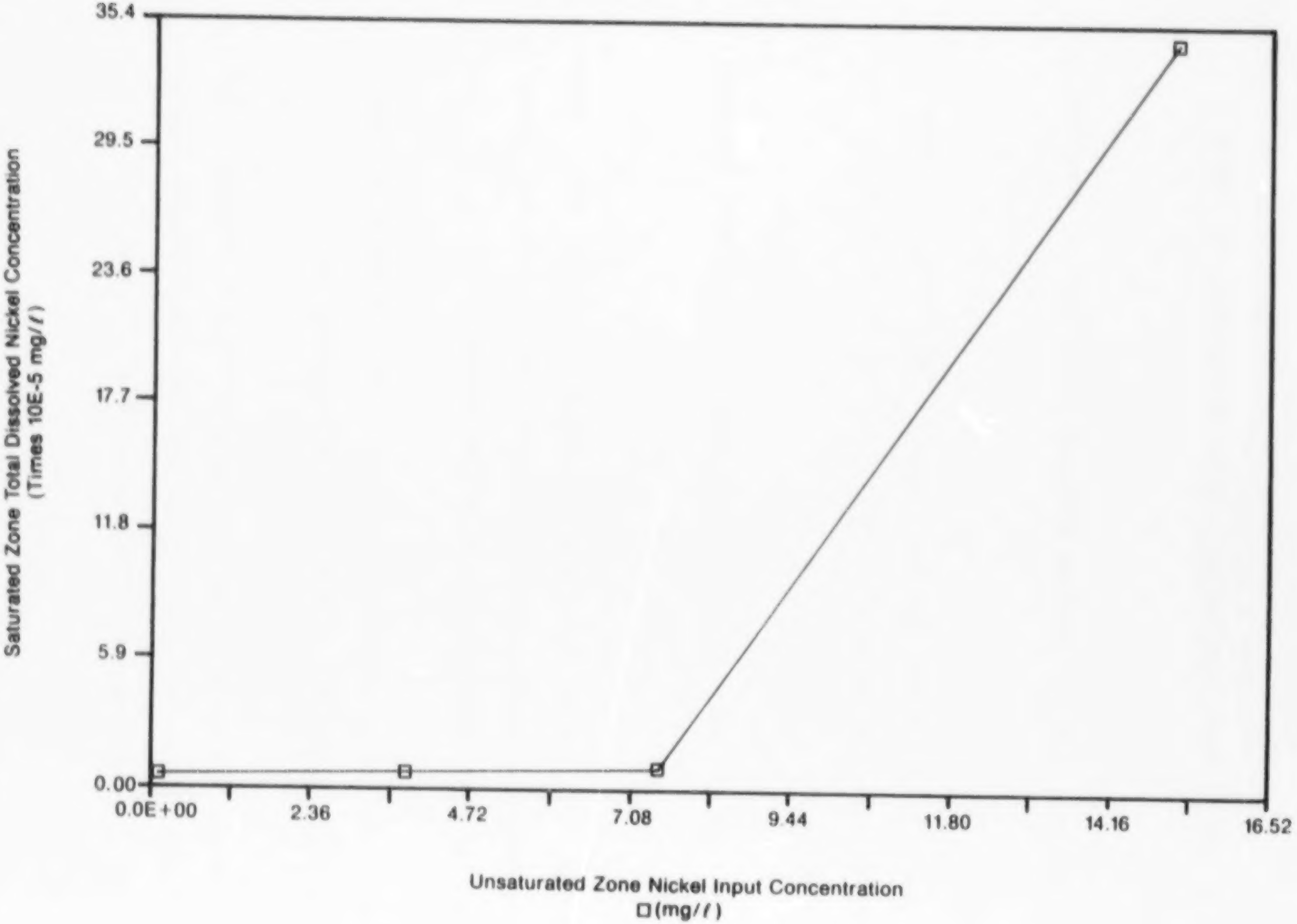


FIGURE B-6f

Saturated Zone Nickel Concentration after Speciation

Conditions: pH = 7.0, Eh = -200 mv

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